CATALYSIS IN THEORY AND PRACTICE

MACMILLAN AND CO., LIMITED
LONDON · BOMBAY · CALCUTTA · MADRAS
MELBOURNE

THE MACMILLAN COMPANY
NEW YORK · BOSTON · CHICAGO
DALLAS · SAN FRANCISCO

THE MACMILLAN CO. OF CANADA, LTD.
TORONTO

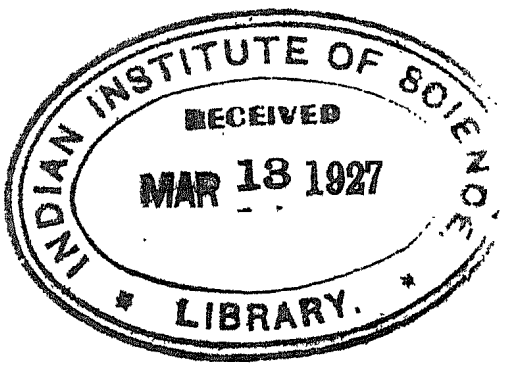
CATALYSIS
IN THEORY AND PRACTICE

BY

ERIC K. RIDEAL
OWEN JONES LECTURER ON PHYSICAL CHEMISTRY, CAMBRIDGE UNIVERSITY, ENGLAND

AND

HUGH S. TAYLOR
PROFESSOR OF PHYSICAL CHEMISTRY, PRINCETON UNIVERSITY, U.S.A.



MACMILLAN AND CO., LIMITED
ST. MARTIN'S STREET, LONDON
1926

107

COPYRIGHT

First Edition 1919
Second Edition 1926

541·395
N26

PRINTED IN GREAT BRITAIN
BY R. & R. CLARK, LIMITED, EDINBURGH

Πάντα ῥεῖ κοὐδὲν ἐν ταὐτῷ μένει

PREFACE TO THE FIRST EDITION

In the development of chemical science during the preceding hundred years, the steady progress in importance which catalytic operations have achieved is distinctly remarkable. Their importance emerges alike in the purely theoretical and in the technical aspects of the subject. In the natural order, also, investigation has shown how predominating a part the catalytic phenomenon plays. From the strictly utilitarian point of view, Industry was not slow to appreciate the advantages to be derived from the employment of agencies which should facilitate and "speed-up" manufacturing processes, nor was there lacking a body of scientific workers who steadily supplied the investigative and theoretical bases upon which such applications could be reared. As the scientific viewpoint developed, the physiologist and biologist rapidly associated the simpler chemical phenomena with the more complex processes operating in living matter. To-day, therefore, catalysis intrudes prominently into all branches of natural science, both pure and applied.

The need for an exposition of the fundamental principles involved in this particular field of general chemistry and of the applicability of such principles in modern life has been widely felt and has offered to the authors the necessary inducement to prepare the present volume. An excellent chapter in Mellor's *Chemical Statics and Dynamics* has formed, hitherto, the sole treatment in English of the theoretical aspects of the problem. From time to time various papers have catalogued the more important practical applications of catalysis. The monograph of Sabatier, *La Catalyse en chimie organique*, deals more particularly with the applications to preparative organic chemistry, with slight reference to the physico-chemical theories involved. Dr. Gertrud Woker has compiled a detailed survey of the theoretical aspects of catalysis and of their application to the problems of analytical procedure, in Margosches's *Sammlung*, entitled, "Die chemische Analyse", vols. xi., xxi., and xxiii. The volume entitled *Unter-*

suchungen im Gebiete der Kinetik der chemischen Reactionen u Katalyse, by the Russian, Orloff, and *La Catalisis Quimica*, by P. Vittoria, are supplementary to the above volumes. From all the sources, to which we wish to acknowledge our indebtedness, we ha freely drawn in an effort to obtain a systematic and comprehensi treatment of the whole subject.

For personal assistance in the compilation of the work we wis to express our thanks to Professor F. G. Donnan, F.R.S., for advi and for stimulating and continuous encouragement, and to Profess W. M. Bayliss, F.R.S., for a kindly criticism of the chapter dealin with Ferments and Enzyme Action.

The diagrams have been drawn by our laboratory assistan Mr. A. Hiscocks, to whom we express our acknowledgments an thanks.

With a subject the literature of which is already so considerab and is increasing so rapidly and continuously, it is not possible to giv an exhaustive summary of the scientific and technical references. Th aim, rather, has been to embody in the text the main lines of develo ment, choosing from the available examples suitable data for th purposes of illustration. It is hoped that such an object has bee achieved. Criticism or additional information relative to the subject treated will be welcomed.

The subject matter of the volume deals with the influence c catalysts in the reactivities of atoms and molecules among themselve In the future, the problems of chemistry will centre more and mor around the intra-atomic reactions and atomic structure. Already the evidence is available that the atoms undergo processes of radio active disintegration at definite but, thus far, unalterable speeds Will the catalytic agencies be found which shall accelerate th velocity of atomic decay and render available the enormous store of intra-atomic energy? Such is a fitting problem for the year that lie ahead.

LONDON, *November* 11, 1918.

INDIAN INSTITUTE OF SCIENCE LIBRARY

PREFACE TO THE SECOND EDITION

PROGRESS in catalytic studies since the first edition of this volume has necessitated a complete revision of the text and the addition of several new chapters.

Advances are recorded in both the theoretical and practical field. The concept of "active" molecules first postulated by Arrhenius is beginning to assume at least the shadow of an objective reality, and the processes of activation explored by the physicist are being earnestly sought for in chemical reactions. In contact catalysis, experimental investigations have yielded a definite concept of the solid catalytic agent, its properties and behaviour, all of which could only be surmised some years ago. In the domain of theoretical homogeneous catalysis, very definite progress in correlating the data of catalysis with the thermodynamic properties of solutions can be recorded, and a commencement has been made in the inquiry as to the conditions of stability of associated complexes and their electronic structure.

In the applied science, the record of a new, high-pressure, catalytic industrial process, the synthesis of methyl alcohol and motor fuels from water gas, will serve to show what further potentialities are latent in the field.

The character of the volume remains the same. No attempt is made to make of it an extensive bibliography of catalytic literature. The rapidity with which the science is growing practically makes that an impossibility. It aims to present a critical survey of the catalytic field from the standpoint of the theory of the subject. It is the belief of the authors that any extension of our theoretical knowledge will cause the practical application to be more readily achieved.

We welcome the appearance of a second edition of Sabatier's monumental work, *La Catalyse en chimie organique*, both in an original French and an amplified English translation. It forms a very valuable complement, we believe, to the present volume, which, we hope, will be of value also to the organic chemist, stressing as it does

the theoretical aspects of the practical preparative data of Sabatie
We also acknowledge our indebtedness to the Reports of the Committ
on Contact Catalysis of the National Research Council, U.S.A., whic
have materially lessened our labours by their frequent surveys
problems with which we are here intimately concerned.

We hope that, in the revised form, the book will receive as kindl
a welcome as met our initial effort. We wish here to acknowledg
our indebtedness to many kind friends for suggestive criticisms an
advice as to the content of this work. It is our hope that the volum
may be a further incentive to research and development in a ver
fruitful field.

LONDON, *December* 1925.

CONTENTS

CHAPTER I

PAGE

EARLY HISTORY 1

CHAPTER II

CRITERIA OF CATALYSIS 11

CHAPTER III

HOMOGENEOUS REACTIONS 23

CHAPTER IV

THE THEORY OF HETEROGENEOUS CATALYTIC REACTIONS . . 59

CHAPTER V

PROMOTERS, MIXED, SUPPORTED, AND PROTECTED CATALYSTS . 98

CHAPTER VI

CATALYST POISONS AND THE INHIBITION OF HOMOGENEOUS CHEMICAL REACTIONS 127

CHAPTER VII

PROCESSES OF OXIDATION 158

CHAPTER VIII

HYDROGEN AND HYDROGENATION 227

CHAPTER IX

PAGE
Dehydrogenation 283

CHAPTER X

Catalysis in Nitrogen Fixation 304

CHAPTER XI

Hydration, Hydrolysis, and Alcoholysis . . . 314

CHAPTER XII

Dehydration 353

CHAPTER XIII

Colloidal Catalysts 380

CHAPTER XIV

Catalysts in Organic Chemistry 400

CHAPTER XV

Catalysis in Electro-Chemistry 424

CHAPTER XVI

Catalysis by Radiant Energy 438

CHAPTER XVII

Catalysis in Analytical Chemistry 468

Index of Names 503
Index of Subjects 513

TABLE OF ABBREVIATIONS EMPLOYED IN THE REFERENCES

Abbreviated Title.	Journal.
Abh. Akad. Wiss. Berlin	Abhandlungen der Königlich Preussischen Akademie der Wissenschaften zu Berlin.
Abh. d. Bunsen Gesellschaft	Abhandlungen der Bunsen Gesellschaft.
Ahrens Sammlung	Ahrens Sammlung.
Amer. Chem. J.	American Chemical Journal.
Amer. J. Physiol.	American Journal of Physiology.
Annalen	Justus Liebig's Annalen der Chemie.
Ann. Chim.	Annales de Chimie.
Ann. Chim. Phys.	Annales de Chimie et de Physique.
Ann. Physik	Annalen der Physik.
Arch. d. Sci. Phys. et Nat. Geneva	Archives de Sciences Physiques et Naturelles, Geneva.
Arch. Inst. Physiol.	Archives de l'Institut de Physiologie.
Atti R. Accad. Lincei	Atti della Reale Accademia dei Lincei.
Beitr. chem. Phys. u. Path.	Beiträge chemische Physik und Pathologie.
Ber.	Berichte der Deutschen Chemischen Gesellschaft.
Biochem. Zeitsch.	Biochemische Zeitschrift.
B.P.	British Patent.
Bull. Acad. Sci. Cracow	Bulletin International de l'Académie des Sciences de Cracovie.
Bull. Acad. Roy. de Belgique	Académie Royale de Belgique—Bulletin de la Classe des Sciences.
Bull. Bur. of Standards	Bulletin of the Bureau of Standards (U.S.A.).
Bull. des Sciences Technol.	Bulletin des Sciences et Technologie.
Bull. Soc. Chim.	Bulletin de la Société chimique de France.
Bull. Soc. Ind. Mulhouse	Bulletin de la Société industrielle de Mulhouse.
Chem. News	Chemical News.
Chem. Rev. Fett-Harz-Ind.	Chemische Revue über die Fett- und Harz-Industrie.
Chem. Weekblad	Chemisch Weekblad.
Chem. Zeit.	Chemiker Zeitung.
Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.

Abbreviated Title.	Journal
Compt. rend. Soc. de Biol.	Comptes rendus hebdomadaires de Séances de la Société de Biologie.
D.R.P.	Deutsches Reichs-Patent.
Edin. Phil. J.	Edinburgh Philosophical Journal.
F.P.	French Patent.
Gazzetta	Gazzetta chimica italiana.
Jahresber.	Jahresberichte über die Fortschritte der Chemie.
Jahresber. Ges. vaterl. Kultur	Jahresbericht der schlesischen Gesellschaft für vaterländische Kultur.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Biol. Chem.	Journal of Biological Chemistry, New York.
J. Chem. Soc.	Journal of the Chemical Society.
J. f. Gasbeleucht.	Journal für Gasbeleuchtung und Wasserversorgung.
J. Gas Lighting	Journal of Gas Lighting.
J. Ind. Eng. Chem.	Journal of Industrial and Engineering Chemistry.
J. Inst. Pet. Tech.	Journal of the Institute of Petroleum Technologists.
J. Physical Chem.	Journal of Physical Chemistry.
J. pr. Chem.	Journal für praktische Chemie.
J. Russ. Phys. Chem. Soc.	Journal of the Physical and Chemical Society of Russia.
Medd. K. Vetenskapsakad. Nobel-Inst.	Meddelanden från Kongl-Vetenskapsakademiens Nobel-Institut.
Monatsh.	Monatshefte für Chemie und verwandte Teile anderer Wissenschaften.
Petroleum Zeit.	Petroleum Zeitung.
Pflüger's Archiv	Archiv für das gesammte Physiolgie des Menschen und der Tiere.
Pharm. J.	Pharmaceutical Journal.
Phil. Mag.	Philosophical Magazine (The London, Edinburgh, and Dublin).
Phil. Trans.	Philosophical Transactions of the Royal Society of London.
Physikal. Zeitsch.	Physikalische Zeitschrift.
Pogg. Ann.	Poggendorff's Annalen der Physik und Chemie.
Proc. Amer. Gas Inst.	Proceedings of the American Gas Institute.
Proc. Chem. Soc.	Proceedings of the Chemical Society.
Proc. Paint Varnish Soc.	Proceedings of the Paint and Varnish Society.
Proc. Phys. Soc. London	Proceedings of the Physical Society of London.
Proc. Roy. Soc.	Proceedings of the Royal Society.
Quart. J. exp. Physiol.	Quarterly Journal of Experimental Physiology.
Rep. Brit. Assoc.	Report of the British Association for the Advancement of Science.
Schweigger's Journ.	Schweigger's Journal für Chemie und Physik.
Seifenfabrikant	Der Seifenfabrikant.

Abbreviated Title.	Journal.
Seifen. Zeit.	Seifensieder Zeitung.
Sitzungsber. K. Akad. Wiss. Wien	Sitzungsberichte der Kaiserlichen Akademie der Wissenschaften in Wien.
Sitzungsber. K. Akad. München	Sitzungsberichte der Königlichen bayerischen Akademie der Wissenschaften zu München.
Soc. Tech. de l'Ind. du Gaz en France	Société Technologique de l'Industrie du Gaz en France.
Trans. Amer. Electrochem. Soc.	Transactions of the American Electrochemical Society.
Trans. Farad. Soc.	Transactions of the Faraday Society.
U.S.P.	United States Patent.
Virchows Archiv.	Virchows Archive.
Wied. Ann.	Wiedemanns Annalen der Physik und Chemie.
Zeitsch. angew. Chem.	Zeitschrift für angewandte Chemie.
Zeitsch. anorg. Chem.	Zeitschrift für anorganische und allgemeine Chemie.
Zeitsch. Elektrochem.	Zeitschrift für Elektrochemie.
Zeitsch. f. Beleucht.	Zeitschrift für Beleuchtung.
Zeitsch. physikal. Chem.	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
Zeitsch. physiol. Chem.	Hoppe-Seylers Zeitschrift für physiologische Chemie.

All temperatures, unless otherwise stated, are in Centigrade.

CHAPTER I

EARLY HISTORY

THE conscious development of catalysis in chemical science dates from the co-ordination by Berzelius, in 1835, of a number of isolated observations made by various investigators in the early decades of the nineteenth century. Berzelius for many years contributed annually to the Swedish Academy of Sciences a report on the progress of the physical sciences during the preceding year. The communication of March 1835, subsequently published as the *Jahresberichte für Chemie*, 1836, contained, *inter alia*, a discussion of the researches of Mitscherlich [1] on the rôle of sulphuric acid in the preparation of ether from alcohol. It was shown by Berzelius that the results of this investigation possessed features common to several investigations of the most diverse character.

The argument as developed by Berzelius may be briefly summarised.[2] "Up to 1800, it was recognised that, besides the normal tendency of bodies to combine, heat and in some cases light could also act in the process of combination. Later, the influence of electricity was recognised, but it was soon seen that chemical and electrical affinities were the same thing, and that heat and light had no other action than to augment and diminish these affinities." A new type of force was involved, however, according to Berzelius, in a number of reactions. Thus Kirchhof had shown [3] that in the conversion of starch to sugar by means of dilute acids, the acid effecting the change remained unaltered. Thénard discovered hydrogen peroxide and showed that in presence of acids the substance was stable. With alkali, however, decomposition set in with evolution of oxygen, which was also facilitated by the presence of substances such as manganese, silver, platinum, gold, and fibrin.[4] Edmund Davy [5] demonstrated that, with finely divided platinum soaked in spirit of wine, ethyl alcohol was oxidised to acetic acid. In 1822 Döbereiner [6] showed that spongy platinum in the cold induced the spontaneous combustion of hydrogen and oxygen,

[1] *Pogg. Ann.*, 1834, **31**, 273.
[2] *Jahresber.*, 1836, **15**, 237; *Ann. Chim. Phys.*, 1836 (iii.), **61**, 146.
[3] *Schweigger's Journ.*, 1812, **4**, 108.
[4] *Ann. Chim. Phys.*, 1818, **9**, 314.
[5] *Phil. Trans.*, 1820, **100**, 108.
[6] *Schweigger's Journ.*, 1822, **34**, 91; 1823, **38**, 321.

and this observation was followed by the discovery of Dulong a Thénard [1] that gold, silver, and even glass possessed the same prope if the temperature of these agencies was sufficiently raised. Fina cites Berzelius, the researches of Mitscherlich show that the convers of alcohol to ether was not dependent on the affinity of sulphuric a for water, since by a proper adjustment of conditions the addition alcohol to sulphuric acid resulted in the evolution of ether and wat the sulphuric acid therefore being analogous to the alkali of Thénard the decomposition of hydrogen peroxide.

Berzelius therefore concludes: "It is then proved that seve simple and compound bodies, soluble and insoluble, have the proper of exercising on other bodies an action very different from chemi affinity. By means of this action they produce, in these bodi decompositions of their elements and different recombinations of the same elements to which they themselves remain indifferent.

"This new force, which was hitherto unknown, is common organic and inorganic nature. I do not believe that it is a force qu independent of the electro-chemical affinities of matter; I believe, the contrary, that it is only a new manifestation of the same; bu since we cannot see their connection and mutual dependence, it w be more convenient to designate the force by a separate name. I w therefore call this force *the catalytic force*, and I will call *catalysis* t decomposition of bodies by this force in the same way that one ca by the name analysis the decomposition of bodies by chemical affinity

The illustrations of catalysis cited by Berzelius in the memo just quoted represented by no means an exhaustive list of the catalyt operations which had up to that time been used and studied. Obvious many of the primitive arts involved unconsciously the application Berzelius's "catalytic force". The production of wine, for examp by fermentation processes dates back to the ancients, though neith sugar nor alcohol appears to have been known, as such, to Plin Berthelot tracing back the rectification of alcohol from wine no furth than the eighth century.[2] The production of acetic acid by ferment tion of wine gave the ancients their earliest acid solvent. The man facture of soap by the action of alkalis on fats also dates back ancient times. Pliny[3] refers to "Sapo, Gallorum hoc inventum and makes it probable that the Romans received from Gaul a Germany a product prepared from animal fat and the aqueous extra of ashes. Ether, which has been attributed to the Arabians, w certainly well known in the Middle Ages, being produced by the acti of sulphuric acid on alcohol. The first exact knowledge of its prepar tion we owe to Valerius Cordus in the sixteenth century. The miner acids were not known until the alchemical era, but the preparation sulphuric acid by setting fire to sulphur admixed with saltpetre is t

[1] *Ann. Chim. Phys.*, 1823 (ii.), **23**, 440; **24**, 380.
[2] *Ann. Chim.*, 1852 (vi.), **23**, 433. [3] *Hist. Nat.*, **28**, 12.

alchemical origination of the catalytic lead chamber process of sulphuric acid manufacture. The identity of the sulphuric acid obtained by the different methods of preparation from alum, from vitriol, and from sulphur and nitre was established by Libavius in the Iatrochemical era, to whom is also to be attributed the first use of the term "catalysis" in a chemical treatise. In the table of contents of his treatise on Alchymia is to be found a section devoted to "Catalysis", but, according to Goldschmidt,[1] examination of the treatise itself fails to reveal anything corresponding with that implied in our modern use of the term. One cannot entirely dissociate the alchemist's search for the "philosopher's stone" from the modern search for suitable catalysts. George Ripple likened the stone to a ferment. The records of the efficacy of the philosopher's stone in the literature of alchemy suggest, moreover, the poisoning of catalysts with which, later, this volume will be largely concerned. Thus, Roger Bacon ascribes to the stone the power to transform a million times its weight of base metal into gold. The more audacious Raymond Lully cites the transformation of ten billion times its weight of base metal. But, with the decay of alchemy, the claims become more modest, or the poisoning effect becomes the more pronounced, for John Price, the last alchemist and gold-maker of the eighteenth century, is but able to chronicle an efficacy of thirty times and one of sixty times the weight of the stone.

Of researches prior to and in the early decades of the nineteenth century concerned with the operation of a catalytic agent and not included in the co-ordination of Berzelius, particular mention might be made of the following. Mrs. Fulhame [2] dealt with the influence of water on chemical reaction, more especially in the reduction of metallic oxides and in the oxidation of carbon monoxide, and clearly demonstrated the necessity for the presence of water, at least in traces, for the production of reaction. The researches of Döbereiner on the combustion of hydrogen and oxygen were preceded by the observations of Sir Humphry Davy [3] on the capacity of platinum wires or foil heated to below redness to promote the combination of oxygen with coal-gas, cyanogen, hydrogen cyanide, alcohol, ether, or naphtha. Erman [4] showed that platinum at a temperature of 50° was sufficient to ignite a mixture of hydrogen and oxygen. Döbereiner's work on the action of cold platinum introduced into the gases was rapidly followed by that of Turner [5] on the action of platinum in promoting the combination of hydrogen with chlorine and other gases, and his unsuccessful attempts to cause preferential combustion.

Impurities such as hydrogen sulphide, ammonia, carbon disulphide, ethylene, and ammonium sulphide were shown to inhibit the activity of platinum. "It was this inefficiency of the platinum sponge on the

[1] *Zeitsch. Elektrochem.*, 1903, **9**, 736.
[2] *An Essay on Combustion*, London, 1794.
[3] *Phil. Trans.*, 1817, **97**, 45.
[4] *Abh. Akad. Wiss. Berlin*, 1818–19, 368.
[5] *Edin. Phil. J.*, 1834, **11**, 99, 311.

compounds of charcoal and hydrogen in mixture with oxygen, while it reacts so remarkably with common hydrogen, and also, though slowly, on carbonic oxide", that suggested to Henry [1] "the possibility of solving by its means some interesting problems in gaseous analysis. I hoped more especially to be able to separate from each other the gases constituting certain mixtures, to the compositions of which approximations had hitherto been made, by comparing the phenomena and results of their combustion with those which ought to ensue, supposing such mixtures to consist of certain hypothetical proportions of known gases." And the conclusion is drawn that, "When the action of the platinum sponge was moderate, only the hydrogen and carbonic oxide were consumed, or at most the olefiant gas was but partially acted upon. From the facts which have been stated, it appears that when the compound combustible gases, mixed with each other, with hydrogen, and with oxygen, are exposed to the platinum balls or sponge, the several gases are not acted upon with equal facility; but that carbonic oxide is most disposed to unite with oxygen; then olefiant gas, and, lastly, carburetted hydrogen. By due regulation of the proportion of hydrogen it is possible to change the whole of the carbonic oxide into carbonic acid without acting on the olefiant gas or carburetted hydrogen." At a temperature of 170° it was further shown by Henry that "when carbonic oxide and hydrogen gases in equal volumes, mixed with oxygen sufficient to saturate only one of them, were placed in contact with the sponge, from the quantity of carbonic acid remaining at the close of the experiment it appeared that four-fifths of the oxygen had united with the carbonic oxide and only one-fifth with the hydrogen", a remarkable result, which was also obtained when excess was used. This extraordinary research represents in many respects a study of catalytic action of the most fundamental importance even at the present day.

The genesis of the modern contact process of sulphuric acid manufacture dates also from the period prior to the Berzelian definition of catalysis. Phillips, a Bristol manufacturer of vinegar, patented [2] the use of platinum, whether of wire or sponge, for the oxidation of sulphur dioxide by means of air. The process was employed at Lille by Kuhlmann in 1883, but was abandoned owing to loss of catalytic activity by the platinum, an inhibiting factor which was not satisfactorily overcome in technical practice until the dawn of the present century.

It is to Faraday [3] that we owe a detailed inquiry into "the power of metals and other solids to induce the combination of gaseous bodies" and into "some very extraordinary interferences with this phenomenon". The researches were initiated in the course of experiments

[1] *Phil. Mag.*, 1825, **65**, 269. [2] B.P. 6069/1831.

[3] *Experimental Researches in Electricity*, 1849, **1**, 165, 6th series, Nos. 564-659; "Everyman's Library", No. 576, pp. 84-111; *Phil. Trans.*, 1834, **114**, 55.

to render efficient the hydrogen-oxygen voltameter, in which Faraday "was occasionally surprised at observing a deficiency of the gases resulting from the decompositions of water, and at last an actual disappearance of portions which had been evolved, collected, and measured. . . . It was found that this effect was not due to the escape or solution of the gas, nor to recombination of the oxygen or hydrogen in consequence of any peculiar condition *they* might be supposed to possess under the circumstances; but to be occasioned by the action of one or both of the (platina) poles within the tube upon the gas around them." It was established that the positive platina plate was more active than the negative, and that with the former, in addition to its rapid action on oxygen and hydrogen, a feebler action was exerted by it on mixtures of nitrous oxide and hydrogen. According to Faraday, mixtures of olefiant gas or carbonic oxide with oxygen, or of equal volumes of hydrogen and chlorine, were not affected by the prepared platina plate.

"Reverting to the action of the prepared plates on mixtures of hydrogen and oxygen, I found that the power, though gradually diminishing in all cases, could still be retained for a period varying in its length with circumstances. . . . The continuance of the action greatly depended upon the purity of the gases used. . . . The act of combination always seemed to diminish, or apparently exhaust, the power of the platina plate."

As a result of his inquiries Faraday concludes that it may be observed of this action, that, with regard to platina, it cannot be due to any peculiar, temporary condition, either of an electric or any other nature: the activity of plates rendered either positive or negative by the pole, or cleaned with such different substances as acids, alkalis, or water; charcoal, emery, ashes, or glass; or merely heated, is sufficient to negative such an opinion. Neither does it depend upon the spongy and porous, or upon the compact and burnished, or upon the massive or attenuated state of the metal, for in any of these states it may be rendered effective or its action taken away. The only essential condition appears to be a *perfectly clean* and *metallic surface*, for whenever that is present the platina acts, whatever its form and condition in other respects may be; and though variations in the latter points will very much affect the rapidity, and therefore the visible appearances and secondary effects of the action, *i.e.* the ignition of the metal and the inflammation of the gases, they, even in their most favourable state, cannot produce any effect unless the condition of a clean, pure, metallic surface be also fulfilled.

"All the phenomena connected with this subject press upon my mind the conviction that the effects in question are entirely incidental and of a secondary nature; that they are dependent upon the *natural conditions* of gaseous elasticity combined with the exertion of that attractive force possessed by many bodies, especially those which are

solid, in an eminent degree, and probably belonging to all; by which they are drawn into association more or less close, without at the same time undergoing chemical combination though often assuming the condition of adhesion; and which occasionally leads, under very favourable circumstances, as in the present instance, to the combination of bodies simultaneously subjected to this attraction. I am myself prepared to admit (and probably many others are of the same opinion), both with respect to the attraction of aggregation and of chemical affinity, that the sphere of action of particles extends beyond those other particles with which they are immediately and evidently in union, and in many cases produces effects rising into considerable importance; and I think that this kind of attraction is a determining cause of Döbereiner's effect, and of the many others of a similar nature."

It will be evident, therefore, that Faraday, in 1833, and prior to the co-ordination by Berzelius of the several examples of catalytic action, had clearly expressed a theory as to the mechanism whereby such action should occur. The theory, it will be observed, confirms the viewpoint expressed by Berzelius in his later publication, that the catalytic force is not independent of the affinities of matter but only a new manifestation of the same.

The retardation caused by admixture of foreign gases on the combination of hydrogen and oxygen was also studied by Faraday, who found that " the order in which carbonic acid and these substances seemed to stand was as follows, the first interfering least with the action: nitrous oxide, hydrogen, carbonic acid, nitrogen, and oxygen ". These did not prevent the action of the plates, " nor was the retardation so great in any case as might have been expected from the mere dilution of the oxygen and hydrogen ". Faraday found that ethylene decreased the action of platinum more than did carbon monoxide; but this result was not confirmed by Henry [1]; Bancroft [2] thinks this was probably due to some impurity in Faraday's ethylene. The retardation by carbon monoxide, however, is well confirmed by both investigators.

Of the explanation of retardation, Faraday writes: " The theory of action which I have given for the original phenomena appears to me quite sufficient to account for all the effects by reference to known properties, and dispenses with the assumption of any new power of matter. I have pursued this subject at some length, as one of great consequence, because I am convinced that the superficial actions of matter whether between two bodies, or of one piece of the same body, and the actions of particles not directly or strongly in combination, are becoming daily more and more important to our theories of chemical as well as mechanical philosophy. In all ordinary cases of combustion it is evident that an action of the kind considered, occurring upon

[1] *Phil. Mag.*, 1836 (iii.), **65**, 329. [2] *J. Physical Chem.*, 1917, **21**, 755.

he surface of the carbon in the fire, and also in the bright part of the ame, must have great influence over the combinations there taking lace."

The student of catalysis no less than, for other reasons, the student f electro-chemistry is deeply indebted to Faraday for this early rientation into the mechanism of catalytic action.

The isolation by Payen and Persoz [1] of the enzyme diastase from ıe extract of barley malt was succeeded by the discovery of emulsin ı bitter almonds by Liebig, and the formulation of a theory of its ıode of action, which, however, in view of the preceding review of araday's work, is wrongly stated by Ostwald [2] to be the first theory f catalytic action.

In propounding a theory of catalytic action Liebig was animated ith the purpose of demonstrating that the Berzelian concept of a ɔecial catalytic force was superfluous. As originally expressed, the ıuse of catalytic action lay in the facility possessed by a body in ɛcomposition or combination of communicating to another body in ɔntact with it the same chemical activity or the same powers of ɔmbination which the body itself possessed. In illustration of this ɔperty, Liebig cited the combustion of a body by bringing it into ɔntact with a body which is itself undergoing combustion, and, in ırther illustration, the solubility of platinum when alloyed with lver in acids in which normally the platinum alone remains insoluble.

The illustrations chosen by Liebig can scarcely be described as ıppy, since, as Berzelius very readily pointed out,[3] numerous researches ıd already shown that a burning body was not necessary for the ɔduction of combustion. Even cold platinum sponge was sufficient ı bring about the ignition and also explosive combustion of hydrogen ıd oxygen. On the other hand, the solubility of platinum when loyed with silver was not to be explained on Liebig's assumptions, ıce, as Berzelius emphasised, solution of platinum was not effected hen present in alloys with iron, copper, zinc, or mercury.

Liebig was therefore constrained to modify his theory of catalytic tion, and did so in reference to the problem of sugar fermentation. ıe hypothesis became one of " molecular vibrations ", communicable, r contact, to another body, thus setting up in the atoms of the second stem similar motions leading to reactions or decomposition. In e particular case of sugar fermentation, this would involve that e decomposing yeast-cells, in the process of decomposition, induce stability in the molecules of sugar which thereby suffer accelerated composition to alcohol and carbon dioxide.

The disadvantage of the Liebig theory lies in its unassailability, ıce no possible test of the theory can readily be devised. It is

[1] *Ann. Chim. Phys.*, 1833 (ii.), **52**, 73.
[2] "Über Catalyse", *Vers. Ges. Deutsch. Naturforscher und Ärzte*, Hamburg, 1901.
[3] *Jahresber.*, 1841, **20**, 452.

comprehensive, and as such has earned considerable popularity, owing to its applicability to numbers of imperfectly understood reactions; but, as Ostwald pointed out,[1] it is of but little use as an auxiliary to scientific research, for the direction and suggestion of new lines of investigation. The theory called forth the following caution from Berzelius: In science, one always loses by plausible explanations published prematurely; the only correct method of attaining certain knowledge is to be found in leaving the incomprehensible until the explanation sooner or later is given by facts which are so clear that divided opinion upon the matter can scarcely arise. The procedure thus recommended by Berzelius was faithfully exemplified in the researches of Schönbein, to whom is due many of the facts of the problem of catalysis which we at present know, but who partook to no extent in the theoretical discussions as to cause.

The action of oxides of nitrogen in the lead chamber process possesses considerable historical interest in regard to catalysis, since the explanation originally put forward by Clément and Désormes [2] involving a series of cyclic reactions, the alternate formation and decomposition of "chamber crystals", may be regarded as the first attempt to explain a catalytic process by what has come to be termed the intermediate compound theory. In all the early discussions of the nature of catalytic processes this case was apparently overlooked. The corresponding explanation of the etherification process by Williamson in 1854,[3] involving the intermediate formation and subsequent decomposition of ethyl sulphuric acid, established the concept of intermediate compound formation and led eventually to its extended application to the theoretical interpretation of catalytic processes in which the stoichiometric relationships were not so definitely established.

In the development of a subject so intimately concerned as is catalysis with the conception of velocity of reaction the researches of Wilhelmy,[4] entitled "On the Law according to which the Action of Acids on Cane-sugar Occurs", call for special reference. The importance of the researches lies in the fact that they were the first successful attempts to study the operation of the time factor in chemical reaction. Wilhelmy showed with reference to the hydrolysis of cane-sugar that the rate of inversion was at any moment proportional to the amount of cane-sugar undergoing transformation, in strict agreement with the mathematical equations which he developed from general considerations. The research, moreover, is the first successful attempt to establish the law of mass action in a quantitative manner. Wilhelmy further studied the influence of temperature and concentration of acid in reference to reaction velocity, without, however, coming to any important conclusions. At the close of his research Wilhelmy remarks: "I must leave it to the chemists to decide, whether and how

[1] *Loc. cit.*
[2] *Ann. Chim.*, 1806, **59**, 329.
[3] *Ann. Chim. Phys.*, 1854 (iii.), **40**.
[4] *Pogg. Ann.*, 1850, **81**, 413, 499.

far the formulæ obtained are applicable to other chemical processes; in any case, all those processes to which one ascribes the operation of a catalytic force seem to me to belong to this class." As Ostwald has pointed out, the research was overlooked by numerous later investigators, and it was not until the attention of men of science had been directed to the work by Ostwald [1] that it was recognised that Wilhelmy is to be designated the discoverer of the laws of chemical reaction velocity, since the formulæ which he put forward were subsequently shown to be applicable to a number of chemical processes. The extension of Wilhelmy's work was undertaken by Löwenthal and Lennsen,[2] who showed that the velocities with which the acids invert cane-sugar is proportional to the strengths of the acids. The influence of temperature on reaction velocity was successively studied by Berthelot,[3] by Harcourt and Esson,[4] and later still by Warder,[5] Urech,[6] van 't Hoff, Arrhenius, and many others.

Ostwald claims to have introduced the concept of reaction velocity as a definite criterion of a catalytic process by his insistence, since 1888, on the point of view that the catalyst is to be regarded as accelerator (or inhibitor) of a reaction already taking place, in contradistinction to the concept that a catalyst can initiate a reaction. In agreement with this idea, the following definition of catalysis was put forward by Ostwald: "Catalysts are substances which change the velocity of a given chemical reaction without modification of the energy factors of the reaction." [7] It is claimed by Ostwald for this change, slight though it appears, that it has yielded important results in the scientific development of the subject, since it has facilitated exact investigation of the magnitude and character of such acceleration. The point of view thus put forward does not enjoy universal acceptance. Schönbein, J. J. Thomson, H. E. Armstrong, and Duhem have all indicated their opinion that a catalyst may actually initiate a reaction.

Of the early efforts in the study of catalysis there remain for consideration those which have reference to the influence of the catalyst on reversible processes. As early examples among these may be cited the researches of Lemoine [8] on the decomposition of hydriodic acid, as a type of a heterogeneous catalysis, and those of Berthelot [9] on the equilibria attained in esterification processes, as a type of homogeneous catalysis.

Lemoine demonstrated that in presence of platinum sponge the decomposition limit at 350° was 19 per cent, attained practically immediately. On the contrary, operating without a catalyst at the same temperature under a pressure of two atmospheres, a limit of

[1] *J. pr. Chem.*, 1884, **29**, 385. [2] *Ibid.*, 1862 (i.), **85**, 321, 401.
[3] *Compt. rend.*, 1864, **59**, 616 *et seq.*; *Ann. Chim. Phys.*, 1869 (iv.), **18**, 146.
[4] *Phil. Trans.*, 1867, **167**, 117. [5] *Amer. Chem. J.*, 1881, **3**, 203.
[6] *Ber.*, 1883, **16**, 762; 1884, **17**, 2165; 1887, **20**, 1836.
[7] *Chemische Betrachtungen*, "Die Aula", 1895, No. 1.
[8] *Ann. Chim. Phys.*, 1877 (v.), **12**, 145. [9] *Bull. Soc. Chim.*, 1879, **31**, 342.

18·6 per cent decomposition was attained, although only after an interval of 250 to 300 hours.

Berthelot established the same independence of the equilibrium state in the esterification of alcohols by acetic acid in the absence, and in presence, of traces of mineral acid catalysts such as hydrochloric or sulphuric acid. At the ordinary temperature the equilibrium state was reached with equivalent initial concentrations of alcohol and acid when 66 per cent of the alcohol had been converted in either case, the time required, however, involving years of contact in the absence of catalyst as opposed to a few hours in presence of the mineral acid. In the subsequent theoretical discussion it will emerge that the rôle of the catalyst in the question of equilibrium has a very considerable significance, and has therefore been the object of numerous investigations. The manifold directions which these have assumed necessitate special and individual treatment not consonant with an historical survey, and consequently further discussion will not be intruded at this juncture.

From 1880 onwards the studies of catalytic reactions rapidly multiplied. They were concerned with all the many-sided aspects of the problem. On one hand, investigations yielded advance in the knowledge of theoretical principles underlying catalytic change. On the other, carefully conducted investigations added to the list of reactions capable of catalytic acceleration, a list which, judging by the investigations of Thénard[1] on hydrogen peroxide decomposition, or by the speculations of Ostwald, might well become comprehensive of all chemical reactions. Catalytic processes were employed with signal success in the studies inaugurated by the theory of electrolytic dissociation of Arrhenius and in the development of modern physical chemistry which resulted from that theory and the theory of dilute solutions of van 't Hoff. At the same time there was developing, constantly and consciously, the application of catalysis to industrial enterprise, which has yielded results the importance of which can be adjudged from a consideration of the manufacture of synthetic indigo, of contact sulphuric acid, of synthetic ammonia, or of the modern hydrogenation of fats.

It is to the many features of all such developments that attention will, in the succeeding chapters, be directed.

[1] *Ann. Chim. Phys.*, 1818, 9, 314.

CHAPTER II

CRITERIA OF CATALYSIS

r the preceding chapter relative to the early history of catalysis it .s been shown that a large number of reactions proceed in the esence of suitable agents, which, following the nomenclature of :rzelius, are called catalytic agents, the reactions themselves being oken of as examples of catalysis. Thus far, however, no exact finition of catalytic action has been laid down, and little has been id as to criteria of catalysis beyond the definition attributed to stwald, in which the acceleration of a reaction by the presence of a ven substance is regarded as a criterion of catalytic action. In order, erefore, to delimit the field of chemical science with which this survey concerned, it is necessary to proceed to an examination of the various sts which may be applied to a given chemical operation in order to certain whether, in the process thereof, the phenomenon of catalysis trudes. The criteria thus laid down it will be advantageous to ustrate by reference to typical examples and to the research work nich has been conducted with a view to verification.

The fundamental characteristic of all catalysed processes is that ey are reactions which, in the thermodynamic sense, are classed as ontaneously occurring processes. That is, they are reactions which cur with diminution of free energy. Any such reaction which is celerated by the presence of an added substance may be classed as a talytic action, and the agent added may be regarded as the catalyst catalytic agent. The catalyst therefore operates to produce equili- ium, in a system removed from the equilibrium state, more rapidly an this would be achieved in the absence of the catalyst. This aracteristic limits fundamentally the range of catalytic study. nus, while it encourages a search for catalysts which will promote e combination of nitrogen and hydrogen to the extent which modern ysico-chemical studies have shown to be possible from the thermo- namic data in question, it discourages definitely a search for celerating agents for reactions opposed to the normal free energy lationships of the reaction system. Search is useless for a catalytic ent which shall transform, for example, large quantities of oxygen,

at room temperature, into ozone, since the equilibrium concentration of ozone in presence of oxygen, at room temperature, is vanishingly small. Similarly, it is not possible, with the aid of a catalytic agent, to achieve, at a given temperature, an equilibrium concentration of a resultant equal to that prevailing at some other temperature, if the equilibrium concentration varies markedly with temperature. More concretely, we may say that, in the production of nitric oxide from nitrogen and oxygen, it is not possible to achieve with the aid of a catalyst, at lower and more practicable temperatures, the equilibrium concentrations of the oxide which are normally obtained at the high temperature of the electric arc. For, such concentrations would be greater than the equilibrium concentrations at the lower temperature concerned, since the combination of nitrogen and oxygen to form nitric oxide is endothermic, and the catalyst would be therefore employed in achieving a reaction in opposition to the normal free energy of the process. It should be demonstrable, in all the numerous types and examples of catalytic processes discussed in the following pages, that they are reactions involving a diminution of free energy, reactions progressing towards the normal equilibrium condition of the system.

The criterion of velocity increase is an essentially practical criterion, for on this is based a differentiation in catalytic efficiency. From the practical standpoint, the addition, to a reaction system, of a substance which has no influence either on the equilibrium or on the speed with which equilibrium is attained is without interest, although from the theoretical standpoint interesting problems might be involved. Catalytic efficiency will be judged either by the relative accelerations produced by equal quantities of added catalytic agents or by the relative concentrations of added agents which are required to produce a given acceleration. The mechanism by which the acceleration is produced in the two cases may be entirely different. Furthermore, relative efficiencies may vary with variation in the physical conditions under which the reaction is carried out. These two factors may be illustrated conveniently by the so-called water-gas reaction,

$$CO + H_2O = CO_2 + H_2,$$

with two catalytic agents copper and oxide of iron. Over the range 200°-300° C. copper is more efficient than iron oxide as a catalyst for this reaction.[1] Above 300° C., however, iron oxide is quite definitely the more efficient, and, in the region of 400°-450° C., equilibrium conversions are readily achieved. With copper, at these temperatures, a relatively low and decreasing efficiency is found. Armstrong and Hilditch show that this varying efficiency and order of efficiency may be attributed to the differing mechanisms whereby the reaction in question is achieved. Whereas, in the case of copper, the products appear to be formed via formic acid as an intermediate stage, in the

[1] Armstrong and Hilditch, *Proc. Roy. Soc.*, 1920, 97A, 265.

presence of iron oxide an alternate reduction of the oxide by carbon monoxide and oxidation of the reduction product by steam apparently occur. It is evident from this, also, that mechanism cannot be involved in the criteria of catalysis.

Certain additional observations of facts in regard to catalytic processes may now be made. The catalytic agent is present in the reaction system on completion of the reaction process. If, therefore, the reaction products be removed and further quantities of the reactants be brought into contact with the catalyst, the process can be repeated and the sequence thereby continued indefinitely. Herein lies one of the principal practical advantages of the catalytic agent, since it ensures that, with minimal amounts of catalyst, large quantities of the reacting substances may be transformed. So long ago as 1806, observation of the cyclic nature of the reaction of oxides of nitrogen in the lead chamber process of sulphuric acid manufacture led Clément and Désormes to this conclusion, which is universally valid in all cases in which the possibility of secondary reactions is excluded. These latter, however, are by no means infrequent, and so it is common in the literature of catalytic agencies to refer to the " life " of a catalyst. This may be stated in a variety of ways, all of which, however, are referable to the ratio of reactants transformed to catalytic material employed.

In illustration of the several points thus raised in connection with the quantity of catalyst required for the transformation of reacting substances, the following examples may be cited. Bredig has pointed out that the combination of hydrogen and oxygen at the ordinary temperature could be brought about by 2·5 c.c. of a colloidal solution of platinum containing as little as 0·17 milligram of platinum, and that, at the outset, the rate of combination was 1·8 c.c. of gas per minute. After a period of time during which 10 litres of gas had undergone combination, it was found that the activity of the colloidal solution was still unimpaired, the velocity of combination being, within the experimental error, identical with that prevailing at the commencement. Mellor [1] cites the observation of Titoff [2] that the presence of 0·0000000000001 N . $CuSO_4$ solution is sufficient to produce a perceptible acceleration of the rate of oxidation of an aqueous solution of sodium sulphite.

Sulphuric acid is the usual catalyst for the dehydration of alcohol to yield ether. As operated in modern technical practice, secondary reactions are practically excluded, so that an initial quantity of sulphuric acid is sufficient for the transformation of large quantities of alcohol. In the laboratory, and also in less modern types of technical plant where the control of the process is by no means so certain, it is a matter of common observation that, in addition to the etherification process, side reactions intrude, manifested by charring of the organic

[1] *Chemical Statics and Dynamics.* [2] *Zeitsch. physikal. Chem.*, 1903, **45**, 641.

material and reduction of the sulphuric acid to sulphur dioxide. In such circumstances the catalyst shows a steadily diminishing efficiency, so that, sooner or later, replacement of the acid becomes necessary. Such an example illustrates the importance of the problem of side-reactions to the main catalytic process in the technical application of catalysis. It will emerge later in the discussion on " catalyst poisons " that in such cases as the contact sulphuric acid process, the synthesis of ammonia and its oxidation to nitric acid, as well as in many other reactions of technical importance, the essentials of success are to a considerable degree governed by the elimination of materials which, by reaction with, or modification of, the catalytic material, suppress practically entirely the activity of the catalyst. Such side-reactions eliminated, however, technical catalysts are oftentimes very long lived. Examples are known of contact masses in sulphuric acid manufacture in which the platinum catalyst has remained efficient during a period of ten years of manufacture, being finally discarded rather by reason of high resistance to the passage of the gases than for loss of catalytic activity.

In heterogeneous catalytic reactions the physical condition of the catalyst may be modified as a result of its participation in the reaction process. In many cases, such change in physical condition is a necessary preliminary to the attainment of full efficiency. Döbereiner's platinum wire becomes covered, after reaction, with a finely divided deposit of metallic platinum, or corroded or pitted in the process of catalysing the hydrogen-oxygen combination. The same phenomenon is observed in the case of the platinum wire forming the gauze used as catalyst in the modern technical process for the oxidation of ammonia with air or oxygen, and Bone has illustrated its occurrence in the employment of silver gauzes in surface combustion processes.

The change in physical state of the catalyst is generally attributed to its activity in a series of cyclic actions in which the material participates, the final reaction of the cycle resulting, however, in the regeneration of the catalytic material in its initial form. Thus, in the well-known action of manganese dioxide in promoting the decomposition of potassium chlorate with evolution of oxygen, it has been observed that if initially a crystalline form of the oxide be employed, the final product is manganese dioxide in the form of a fine powder. The researches of Sodeau [1] have associated this change in physical state with the participation by the manganese oxide in the process of chlorate decomposition. Langmuir [2] compares the changes that occur in the surfaces of metals used as catalysts with the " offsetting " of tantalum filaments, or improperly made tungsten filaments, when run in lamps on alternating current. The offsetting consists of a slipping of the crystals of the metals along the boundary planes, and, in extreme cases,

[1] *J. Chem. Soc.*, 1900, **77**, 137, 717; 1901, **79**, 247, 939; 1902, **81**, 1066.
[2] *Trans. Farad. Soc.*, 1922, **17**, 618.

it leads to a disintegration of the structure of the metal. The effect has been shown to be dependent upon the rapidity of temperature fluctuation. The same is true of the surface of the target in an X-ray tube run on alternating current. Introduction of gases intensifies the effect. Langmuir concludes that, in all these cases, the disintegration is to be ascribed to sudden fluctuations in temperature between adjacent atoms in the metal.

Catalysts and equilibrium.—We may now turn our attention to the question of equilibrium in catalysed reactions. It will be useful to consider the problem fundamentally, in reference to a perfectly general reaction. Let us assume a reaction between a moles A and b moles of B to yield c moles of C and d moles of D. Let a concentration of x moles of the catalyst X be present throughout the reaction process. We may express this process by the equation

$$aA+bB+x\dot{X}=cC+dD+x\dot{X}.$$

For a dilute gaseous system, obeying the gas laws, it may readily be shown, either kinetically or thermodynamically, that, at equilibrium,

$$K_p=\frac{P_C^c\times P_D^d\times P_X^x}{P_A^a\times P_B^b\times P_X^x}=\frac{P_C^c\times P_D^d}{P_A^a\times P_B^b}, \quad . \quad . \quad . \quad (1)$$

where P refers to the partial pressure of the given species at equilibrium. It can readily be seen that the right-hand member of Expression (1) is identical with the equilibrium expression for the non-catalysed reaction, which signifies that the value of K_p is identical for both catalysed and non-catalysed reactions in a dilute gaseous system.

Similarly, for the same reaction occurring in an ideal solution, it can also be shown that, at equilibrium,

$$K_M=\frac{M_C^c\times M_D^d\times M_X^x}{M_A^a\times M_B^b\times M_X^x}=\frac{M_C^c\times M_D^d}{M_A^a\times M_B^b}, \quad . \quad . \quad . \quad (2)$$

where M refers to the mol fractions of the several species at equilibrium. Correspondingly, for a very dilute solution in which the laws of dilute solution hold, we obtain

$$K_C=\frac{C_C^c\times C_D^d\times C_X^x}{C_A^a\times C_B^b\times C_X^x}=\frac{C_C^c\times C_D^d}{C_A^a\times C_B^b}, \quad . \quad . \quad . \quad (3)$$

where C refers to the molecular concentrations of the several species at equilibrium. In these cases, also, it is manifest that the equilibrium constants remain unchanged in the catalysed process or that the catalyst does not alter the position of equilibrium in systems composed of ideal or very dilute solutions.

Actual reaction systems deviate to a greater or less degree from the ideal systems which we have just discussed. For this reason, it has become general in recent years, in discussing problems of chemical

equilibrium, to employ the concept of the activity of a reaction species in place of one or other or all of the concepts possible with ideal systems.[1] The activity of a species may be defined essentially by the equation

$$F_A = RT\ln a_A + C_A, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where F_A is the molal free energy of the substance A under given conditions, a_A is its activity, and C_A is a constant which may be arbitrarily defined. The increase in free energy when a substance changes from one set of conditions to another is given from Equation (4) by the expression

$$F_{A'} - F_A = \Delta F_A = RT\ln\frac{a_{A'}}{a_A}, \quad . \quad . \quad . \quad . \quad (5)$$

where a_A and $a_{A'}$ represent the activities in the initial and final stages respectively and ΔF_A represents the increase in free energy accompanying the change. The essential criterion of a condition of equilibrium in any system at constant temperature is that the free energy change accompanying any process occurring shall be zero. For the reaction,

$$aA + bB = cC + dD,$$

at the condition of equilibrium,

$$aF_A + bF_B = cF_C + dF_D. \quad . \quad . \quad . \quad . \quad (6)$$

By combining Equations (4) and (6) we therefore obtain

$$aRT\ln a_A + aC_A + bRT\ln a_B + bC_B = cRT\ln a_C + cC_C + dRT\ln a_D + dC_D \quad (7)$$

or

$$aC_A + bC_B - cC_C - dC_D = RT\ln\frac{a_C^c \times a_D^d}{a_A^a \times a_B^b}, \quad . \quad . \quad (8)$$

or, since by definition the quantities on the left-hand side are constant, we may write for any given temperature

$$K_a = \frac{a_C^c \times a_D^d}{a_A^a \times a_B^b},$$

where K_a may be termed the equilibrium constant in terms of the activities of the reacting constituents. This equation is independent of any simplifying assumptions and may be regarded as perfectly general for any chemical reaction.

Now this equation has been derived from considerations of the initial and final states of the system independently of any mechanism whereby the process is achieved. Hence it follows that the activity constant Ka and the free energy change for the reaction must be

[1] For a general treatment of the concept of activity, see Taylor, *Treatise on Physical Chemistry*, chapters viii. and xii. (D. van Nostrand & Co., New York, 1924; Macmillan & Co., London, 1925); or Lewis and Randall, *Thermodynamics and Chemistry* (McGraw-Hill Co., 1923).

unaffected by the presence of any substance occurring on both sides of the equation, provided the equation is otherwise unchanged. This will be true for a gaseous mixture passing over a solid catalyst which is unchanged on completion of the reaction process. The equilibrium partial pressures of the gases issuing from the reaction zone will be identical with those which would be yielded at equilibrium from the same gas mixture in absence of a catalyst. In all cases of this type it is clear that the catalyst cannot affect the equilibrium in the gas phase. *No case is known in which a change in equilibrium has been experimentally demonstrated in reactions of this type.*

In homogeneous systems involving a catalyst it is, however, possible that the equilibrium concentrations of a reaction system may be modified by the presence of a catalyst. It is possible to indicate how this occurs. If the activity of the catalytic agent remains unchanged throughout the reaction, the derivation of Equation (9) indicates that the equilibrium constant K_a remains unchanged in presence of the catalyst. The catalyst, however, may have widely varying effects on the activities of the several reactants; in such case, the mol fractions or the molecular concentrations of these several reactants may have appreciably different values from those obtaining in the absence of a catalyst. It is to this varying effect of a catalytic agent on the activities of the individual reacting species that most of the abnormalities in the determination of equilibria in the presence of catalysts are to be attributed. The effect is particularly apt to occur in equilibria which involve electrolytes either as reactants or as catalysts.

Equilibrium determinations in processes of ester hydrolysis may be cited in illustration of this factor. Jones and Lapworth [1] investigated the equilibrium constant in the hydrolysis of ethyl acetate, using hydrochloric acid as catalyst. It was found that the value obtained for the equilibrium constant in terms of concentrations of the reacting species varied according to the amount of catalyst employed. The appended diagram (Fig. 1) gives a plot of the values of the apparent equilibrium

$$\Psi = \frac{[H_2O][CH_3COOC_2H_5]}{[C_2H_5OH][CH_3COOH]},$$

where the brackets indicate mol fractions. It will thus be seen that the value of $\Psi(=4)$ obtained by Berthelot and Paen de St. Gilles for such homogeneous liquid systems in presence of traces of acid catalyst, rises steadily with increasing concentrations of hydrochloric acid to values in the neighbourhood of 9. This is to be ascribed to the influence of the acid on the activity of the water, and, probably to a lesser extent, the other constituents. The activities of these constituents are then no longer proportional to their mol fractions. Rising values are obtained for Ψ. If the equilibrium constant Ka were

[1] *J. Chem. Soc.*, 1911, **99**, 1427.

calculated from the several activities in presence of varying con centrations of catalyst, a real constancy would be observed. Simila measurements by Armstrong and Worley [1] also show the dependenc of the end-point in acid hydrolysis of esters on the concentration c acid catalyst employed. The variations observed are determined b the influence of the acid on the activities of the several reacting species The introduction of the concept of activity into the mathematica treatment of reaction velocity has been given most comprehensively by Brönsted.[2] Details of this will be given in a later chapter on th kinetics of homogeneous catalytic actions. Bjerrum [3] has pointed out that Brönsted's equation, involving activities of the severa

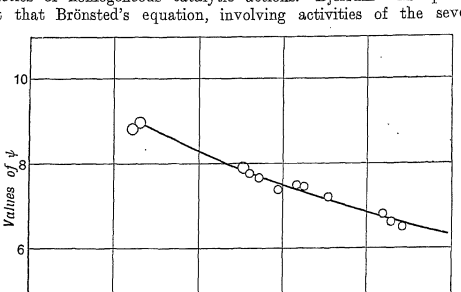


FIG. 1.

molecular species, really involves the concentration of a reacting complex formed by collision of these reacting species.

The more closely a reaction system approximates to that of an ideal system, whether gaseous or in solution, the more nearly independent of either the catalyst employed or the concentration of catalyst does the equilibrium become. As the condition of ideality is approached, the more closely proportional are activity and concentration. That this is approximately realised in some circumstances is evident from the researches of Koelichen [4] on the reversible transformation of acetone to diacetonyl alcohol

$$2CH_3COCH_3 = CH_3COCH_2 \cdot C(CH_3)_2OH.$$

[1] *Proc. Roy. Soc.*, 1912, **87A**, 604.
[2] See especially *Zeitsch. physikal. Chem.*, 1922, **102**, 169.
[3] *Zeitsch. physikal. Chem.*, 1923, **108**, 82. [4] *Zeitsch. physikal. Chem.*, 1900, **33**, 129.

The reaction is catalytically accelerated by hydroxyl ions. The same equilibrium state is attained from either side by such varied agents as ammonia, triethylamine, tetraethyl ammonium hydroxide, and sodium hydrate. Turbaba,[1] also, varied the catalytic agent in the aldehyde-paraldehyde equilibrium, showing that with hydrochloric acid, sulphur dioxide, oxalic acid, zinc sulphate, and other agents the proportion transformed was independent of the nature and quality of the catalytic agent.

There are few direct experimental demonstrations that, in gaseous reactions at a solid surface, the equilibrium position is unchanged. Lemoine's data on hydrogen iodide decomposition at a platinum surface and in absence of such have already been cited in the preceding chapter. Of indirect evidence, however, the literature is full. Every case in which a shift of equilibrium has been suspected has been shown, on closer examination, to be quite normal. Thus, Jellinek [2] suspected that ammonia in excess of the normal equilibrium concentrations might be obtained from nitrogen-hydrogen mixtures in presence of catalytic iron. A most careful study by Larsen [3] has failed to reveal any indication of this whatever. It was suspected by some that the experiments of Milligan, Chappell, and Reid [4] on esterification of alcohol-acetic acid vapours in presence of silica gel indicated a shift of the esterification equilibria, since yields considerably in excess of 66 per cent ester were obtained. This suspicion was unfounded. It arose from a confusion of the equilibrium state in liquid system with that in the vapour phase. Berthelot and Paen de St. Gilles had shown that, in liquid system, the equilibrium position lay in the neighbourhood of 66 per cent ester formation from equimolecular quantities of alcohol and acetic acid. But, as was recently shown by Edgar and Schuyler,[5] in the vapour phase, the equilibrium point is much more markedly on the ester side.

There exists, however, a wealth of indirect evidence that the solid catalyst does not shift the equilibrium in a gaseous reaction. The concordance which exists between the thermodynamic calculations of equilibrium in a variety of gas reactions and the direct experimental measurements of the equilibrium, most of which have been achieved with the aid of catalytic agents, is at once a convincing proof that equilibrium is independent of the catalyst. Thus, for example, the equilibrium in the Deacon chlorine process as determined by Lewis [6] and by von Falkenstein [7] with the aid of catalytic agents, may be harmonised completely with the thermodynamic data for the process. Or, alternatively, the values obtained for the equilibrium in this reaction may be utilised to evaluate free energy functions of the reacting species, which data may in their turn be used for other calcula-

[1] *Zeitsch. physikal. Chem.*, 1901, **38**, 505.
[2] *Zeitsch. anorg. Chem.*, 1911, **71**, 121.
[3] *J. Amer. Chem. Soc.*, 1923, **45**, 2918; 1924, **46**, 367.
[4] *J. Physical Chem.*, 1924, **28**, 872.
[5] *J. Amer. Chem. Soc.*, 1906, **28**, 1380.
[6] *J. Amer. Chem. Soc.*, 1924, **46**, 64.
[7] *Zeitsch. physikal. Chem.*, 1907, **59**, 133.

tions, all of which by a system of check and cross-check can be shown to be in complete agreement. It is in this manner that the most decisive conclusion as to independence of equilibrium and catalyst in such gaseous systems can be achieved. The number of such examples is steadily increasing in the thermodynamic literature.

There follows from this discussion of the catalyst and equilibrium the very practical conclusion that, in a reversible process, the catalyst must accelerate both the forward and backward reactions. In such systems as show no shift of equilibrium with catalyst employed, the same proportionate acceleration will be produced in the inverse reactions. A hydrogenation catalyst will also be efficient in the reverse dehydrogenation. An esterification catalyst will operate also as an agent for hydrolysis of the ester. Numerous examples of this feature will be found in the subsequent chapters.

Solvents and catalysis.—What has been said in the preceding section with respect to the influence of the catalyst on the activities of the several reacting species, and therefore upon the position of equilibrium, can be applied also to the influence of the so-called "indifferent" constituents of the reaction system. Among these "indifferent" constituents the solvent is of first importance. So long as the system is ideal the solvent will be without influence on equilibrium. But, in so much as the solvent or any "indifferent" constituent exercises an influence on the activities of the reacting species, by just so much will its influence on the position of equilibrium be felt. There may exist a whole series of systems in which an added agent will vary at the one extreme from a catalyst, normally so called, to the other extreme in which it is commonly regarded as a solvent; and there will be nothing in principle to distinguish the catalyst in the one solution from the solvent in the other. Thus, a little ether may act in benzene solution as a catalyst for the reactions of the Grignard reagent.[1] By increasing the concentration of the ether continuously, a state of affairs may be obtained in which the ether may justly be regarded as the solvent. In principle or mechanism nothing has been changed. Only in its quantitative aspects has the system undergone change. In each case, reaction will be measured by the activities of the several molecular species.

Since the activity of a substance in solution can only attain certain limiting values dependent largely on the solubility of the species in the given solvent, it is apparent that, from this cause, a solvent may exercise a directive influence on the course of reaction. Thus, in aqueous solution, potassium iodide precipitates mercuric iodide from a solution of mercuric chloride. In acetone solution, on the contrary, mercuric iodide is quite soluble, while potassium chloride is insoluble; hence, addition of mercuric chloride precipitates potassium chloride from acetone solutions of potassium iodide.

[1] Tschelinzeff, *Ber.*, 1905, **38**, 3664.

The problem of the solvent in the reaction process may also be examined from the standpoint of the solvation of the reacting species. If a reactant, A, undergoing change, forms, in a solvent S, a solvated molecule, the equilibrium condition being represented by the equation

$$A + nS = A \,.\, nS,$$

the solvent may exercise a profound influence on the rate of change. If unsolvated A alone undergoes reaction, then presence of the solvent S will lower the specific rate of reaction. If the solvated molecules, $A \,.\, nS$, are reactive constituents, several possibilities may arise. The observed reaction rate will depend on the value of n, which will influence the reactivity of the solvated reactant. The rate may also vary with the nature of the solvent S, and, whether due to the reactivity of either A or $A \,.\, nS$, the rate will also depend on the value of the equilibrium constant in the above solvation equilibrium.

Bjerrum has discussed some of these factors in a recent paper.[1] He points out that the enhanced catalytic activity of hydrogen ions in presence of neutral salts, first noted by Arrhenius, can be explained on the basis of varying hydration of the ion. If the ion in the intermediate complex formed by collision of the reacting species and the hydrogen ion have a smaller water content than the ion in the solution, the Arrhenius effect must result. Bjerrum points out that, if the difference in the two amounts to n moles of water, then the catalytic activity will increase, with decreasing vapour pressure of the solution p, to an extent proportional to $(p_o/p)^n$, where p_o is the vapour pressure of pure water.

Bjerrum further points out that, besides these catalytic effects which may be associated with the formation of definite chemical compounds, and in which the catalyst, so to say, opens up a number of parallel reaction paths, there are certainly cases where the presence of materials foreign to the actual reaction process may actually exert an influence on the reaction speed without actually entering into combination with the reactants. These act by virtue of the molecular forces which they exert on the reacting complex, changing its form without the production of a chemical compound. A deformation of the reaction complex may occur which may have marked influence on the velocity of rearrangement of the complex. There is some evidence that such deformation catalysts are present in some catalytic gas reactions. Bjerrum points out that the relationship between deformation and activity will be slight. The activity of a substance at the same concentration is known to be greater in poor solvents than in good solvents. But it cannot thereby be concluded that the substance will react more rapidly in the poor solvent. Rather should one conclude that the reaction will proceed more rapidly in the good solvent,

[1] *Zeitsch. physikal. Chem.*, 1923, **108**, 82.

because, in this case, the greater solubility is an index of greater molecular forces which may influence the velocity of change by deformation.

Menschutkin[1] attempted to trace a relationship between the dielectric constant of the solvent medium and the velocity of interaction of triethylamine and the ethyl halides in various solvents. Some of his results are recorded in the following table :

Solvent.	Velocity Constant.	Dielectric Constant.
Hexane	0·00018	2·6
Xylene	0·00287	2·6
Benzene	0·00584	2·6
Ethyl alcohol	0·0366	21·7
Methyl alcohol	0·0516	32·5
Acetone	0·0608	21·8
Benzyl alcohol	0·1330	10·0

It is evident from this table that this physical property alone is inadequate to explain the whole of the variation in velocity.

[1] *Ber.*, 1882, **15**, 1818 ; *Zeitsch. physikal. Chem.*, 1887, **1**. 611 : 1890, **5**, 589 ; 1890, **6**, 44.

CHAPTER III

HOMOGENEOUS REACTIONS

Gas reactions.—The problem of the mechanism of homogeneous gas reactions is in reality not so simple as would be imagined from a direct interpretation of the " order " of the reaction.

There are, for example, numerous examples of reactions which are apparently unimolecular in character, and it was, as we shall have occasion to observe, on the hypothesis that a unimolecular constant for the reaction velocity was a true criterion of a unimolecular reaction that led Perrin to his formulation of the radiation hypothesis of chemical action. Apart from the radioactive transformations, however, very few true unimolecular reactions exist. The decomposition of phosphine examined by Trautz and Bhandarkar,[1] which at one time was taken as the classical example of a unimolecular reaction, has been shown by Hinshelwood[2] to be a heterogeneous reaction. On the other hand, the decomposition of nitrogen pentoxide investigated by Daniels and Johnston[3] has recently been shown by Hirst and Rideal to depart from the unimolecular law at pressures below 0·25 mm., but become unimolecular again at very low pressures. An interesting field for investigation would be the dissociation of such compounds as nitrogen tetroxide, of the diatomic molecules of the halogens, and the thermal ionisation of vapours, from the point of view of the order of the reaction. Whilst the pseudo-unimolecular character of a number of decompositions or dissociations evidently requires explanation, the rarity of true unimolecular reactions is significant.

In the case of bimolecular reactions two points of great interest emerge from observations on the reaction velocities at various temperatures. It is found that the number of molecules reacting per c.c. per second falls far short of the number of actual collisions effected between the molecules of the reacting species. From this observation the division of collisions into " effective ", where reaction results, and " ineffective ", or those undergoing ideal elastic collision, may be made. Again, as pointed out by Arrhenius, the influence of

[1] *Zeitsch. anorg. Chem.*, 1919, **106**, 95. [2] *J. Chem. Soc.*, 1924, **125**, 393.
[3] *J. Amer. Chem. Soc.*, 1921, **43**, 53.

temperature on bimolecular reactions is most marked. It is found that the temperature coefficients of chemical reactions are always relatively high, the velocity increasing exponentially with the temperature. The number of collisions per c.c. per second, according to the kinetic theory of gases, is given by the equation

$$N_0 = 2N_1N_2\sigma_1\sigma_2\sqrt{2\pi RT\left(\frac{1}{m_1}+\frac{1}{m_2}\right)},$$

where N_1N_2, $\sigma_1\sigma_2$, m_1, m_2 are the numbers, molecular diameters, and masses of the reacting molecules; it is clear that the exponential increase in the number of effective collisions with the temperature is much greater than the comparatively small increase in the number of total collisions. These results, and more especially considerations based upon the influence of temperature on processes of esterification and hydrolysis in solution, led Arrhenius [1] to the concept of "active" molecules.

According to Arrhenius we must postulate in a reacting species an equilibrium existing between active and inactive molecules:

$$A \rightleftarrows A'.$$

Active molecules on collision produce chemical reaction, inactive molecules ineffective or elastic collision. The conversion of the inactive to the tautomeric active form requires the supply of energy the energy of activation, or the critical energy increment, the magnitude of which, as we shall see, can be determined in certain cases from the temperature coefficient of the reaction.

An adequate interpretation of the simple bimolecular reaction requires an analysis of the mechanism of activation and the source from which this energy required for activation is drawn. There is, however, in addition, a third complicating factor to be considered in such reactions, which can best be exemplified as follows. The heat of dissociation of hydrogen is *ca.* 84,000 per grm.-molecule, or $1{\cdot}37\ 10^{-19}$ cal. per molecule. When two hydrogen atoms approach one another even at very slow speeds to effect union to a molecule, the energy of dissociation has to be liberated before the hydrogen molecule can exist. It is clear that, in the case of a "head on" collision, combination is impossible; for, if the atoms are moving towards one another with identical speeds, before formation of the molecule is possible, both the heat liberated in the reaction and the kinetic energy originally possessed by the atoms have to be dissipated in some way. Two methods of dissipation suggest themselves: the energy may be dissipated in the form of radiation, or a simultaneous collision with a third molecule or atom may take place, and this third member may be shot off again with the excess energy in some form. As we shall have occasion to note, if radiation is emitted in such bimolecular reactions

[1] *Zeitsch. physikal. Chem.*, 1889, 4, 22; 1899, 28, 317.

it is certainly not monochromatic in character; on the other hand, evidence for the removal of the excess energy by a third molecule or atom in the internal form—for example, in the combination of sodium and iodine by sodium atoms—is by no means scanty. It would appear by no means improbable that termolecular reactions, or at least two bimolecular reactions occurring in sequence in a short time interval, are in reality by far the most common.

Although, as we have seen, recombination of atoms can only occur either through the mechanism of a termolecular reaction, or, if bimolecular, through the emission of radiation, certain other types of true bimolecular reactions are possible. In the case of decomposition of complex molecules by bimolecular collision, if the decomposition be an endothermic process, the difficulty to which attention has been drawn does not arise, whilst if the decomposition be exothermic the products of reaction can evidently dissipate the energy in a kinetic manner.

Again, it is conceivable that the union of complex molecules to one another or to atoms may occur, such as the union of atomic oxygen, chlorine, or hydrogen, to their respective molecules, through the agency of true bimolecular reactions, for, although energy in excess of the critical amount required for decomposition has to be dissipated, a mechanism of dissipation is provided in the third atom in the complex molecule.

We have referred to the fact that in the union between atoms either radiation must be emitted or termolecular collisions must occur, the third body, either atom or molecule, serving as an energy dissipator. Since reaction does not occur without such collisions, we may consider this to be a simple case of true catalytic action. The researches of Bonhoeffer [1] on the combination of hydrogen atoms and of Bodenstein and Lütkemeyer [2] on the combination of bromine atoms, indicate that these reactions proceed very much more slowly than anticipated on the assumption of simple bimolecular collisions effecting combination. Only one in every thousand of such collisions is effective, and this may well be termolecular. Beutler and Polanyi,[3] however, have shown that reaction between sodium atoms and halogens and halides may occur with an efficiency of 1 collision in 100, and 10^4 times more rapidly than can be accounted for by triple collisions.

It is interesting to examine how far we can investigate the operation of such catalytic action. It is clear that if the catalyst dissipates the energy in a kinetic manner that recombination of atoms should take place very much more rapidly in the presence of an indifferent gas, for the number of termolecular collisions will be increased. In reversible reactions the augmentation of the velocity of association by the indifferent gas should be accompanied by the augmentation of

[1] *Zeitsch. physikal. Chem.*, 1924, **113**, 199. [2] *Ibid.*, 1924, **114**, 208.
[3] *Naturwissenschaften*, 1925, **13**, 711.

velocity of dissociation, for the equilibrium will be unaffected by its presence. To take a concrete example, if the rate of union of chlorine atoms be facilitated by a neutral gas, the rate of dissociation of the chlorine molecules must likewise be affected, since the equilibrium conditions defined by

$$K_p = \frac{[Cl]^2}{[Cl_2]}$$

remain unaffected. No crucial test of this hypothesis has been made.

We may also consider that the catalytic function of the third atom or molecule is to dissipate the energy in an internal and not kinetic form, and it is only those substances which can acquire this internal energy which act as catalysts. As an example may be cited the union of sodium and iodine atoms effected by the volatilisation of sodium iodide in a hot bunsen flame and cooling the products of dissociation. An examination of the spectrum reveals the presence of the sodium *D* lines but not those of the ionised iodine.

The values of the heats of reaction of the various possible changes are given below.

$$\begin{aligned}
&Na\ gas + I\ gas = Na\ I + 112{,}000.\\
&Na^{\cdot} + I' = Na\ I + 144{,}000.\\
&Na\ gas + {}^1/_2 I_{2\ gas} = Na\ I + 94{,}500.\\
&Na^{\cdot} + (e) \longrightarrow Na + 48{,}500.\\
&I' = I + (e) - 82{,}000.\\
&I = I^{\cdot} + (e) - 185{,}000.
\end{aligned}$$

It is clear from the data presented that the energy dissipated in the union of sodium and iodine atoms will be sufficient to ionise sodium atoms but not iodine; thus the sodium may be regarded as a catalyst but not iodine for the union of sodium and iodine atoms by removing 48,500 out of 112,000 calories in the form of internal energy which is afterwards re-emitted as visible radiation.

Whilst a number of supposedly homogeneous gas reactions have during the past few years been shown to be heterogeneous in that the reactions may occur entirely on (*e.g.* ethylene and the halogens) or commence at (hydrogen and chlorine) the walls of the containing vessel, it cannot be said that the operation of a homogeneous catalytic gas reaction has been studied in detail. It is possible that the catalytic influence of small traces of water vapour examined by Baker in such reactions as the dissociation of ammonium chloride or the union of carbon monoxide and oxygen may prove to be true cases of homogeneous catalysis; yet, as we shall note, in the case of the hydrogen chlorine combination, it is possible that surface action intrudes. Nevertheless, the study of uncatalysed homogeneous gas reactions reveals some of the most interesting peculiarities associated with chemical reactions.

The energy of activation or excitation.—As we have noted,

Arrhenius was led to the concept of active and inactive molecules in which the equilibrium between these two tautomeric forms of the same substance shifted in favour of the active form with rise in temperature. This concept was subsequently extended by Arrhenius to explain the mechanism of catalytic influence, the addition of the catalyst being presumed to bring about an increase in the concentration of the active form.

The alteration of the velocity coefficient with the temperature could be formulated in the expression

$$\frac{d \log K}{dT} = \frac{E}{RT^2},$$

E being the energy required to transform one gram-molecule from the inactive to the active state.

It will be noted that Arrhenius makes no assumption as to the source of the energy of activation but simply postulates the existence of these two tautomeric types as well as a dynamic or mass law equilibrium between them.

Marcelin [1] advanced the problem a stage further by deducing from the Maxwell-Boltzmann principle of the distribution of energy an expression similar to that of Arrhenius. On the assumption that the internal energy of the molecules varies in conformity with the laws of statistical mechanics, and that a molecule reacts when it has acquired internal energy E in excess of the normal,[2] he showed that the rate of variation of the velocity constant with the temperature would be expressed by the relationship

$$\frac{d \log K}{dT} = \frac{E_c}{RT^2}.$$

Marcelin's E_c, termed the critical energy increment, is thus identical with the energy of activation E postulated by Arrhenius.

The concept of Marcelin that it is the "internal energy" of a molecule which renders it active, is similar if not identical with the conception of the "excited" molecule of the physicist.

The probability that a molecule will react after it has gained internal energy E_c may increase with augmentation of this internal energy content; we shall then obtain, adopting again the hypothesis of a statistical distribution in internal energy,

$$\frac{d \log K}{dT} = \frac{E_c + RT}{RT^2},$$

since E_c is usually great compared to RT; to test this modification

[1] *Compt. rend.*, 1914, 158, 161.

[2] G. N. Lewis and Smith (*J. Amer. Chem. Soc.*, 1925, 47, 1513) assume that E_c is the internal energy of a reactive molecule, not the excess above the average internal energy content; there is no justification, however, for this assumption.

of the equation for the temperature coefficient of reaction velocity would require experimental data of a high order of accuracy.

Since the energy of excitation or activation is internal in character, we must inquire how this energy is acquired, a point on which neither Arrhenius nor Marcelin expressed any opinion.

Two methods have been suggested, one by the absorption of radiation, the other by means of molecular collision of a special type.

The radiation theory of activation.—In 1906 Trautz,[1] and independently both McC. Lewis [2] and Perrin,[3] suggested that the energy of excitation might be obtained from radiation normally existing and flowing through the reaction system.

Perrin was led to this point of view by consideration of the mechanism of unimolecular actions. For such actions the probability of a particular isolated molecule decomposing within the next second is invariant, since the velocity constant is independent of the concentration. The critical energy increment can evidently only be supplied by some non-material type of energy transfer such as radiation, either in the infra-red or other portion of the spectrum. Trautz and Lewis were led to the same view by a supposed analogy between photochemical and thermochemical reactions. The extraordinary simplification which would be introduced into chemistry if chemical activation were always produced by the absorption of radiation is the great attraction of the radiation hypothesis.

It was suggested by Trautz and McC. Lewis that the activating radiation was monochromatic in character, and that its frequency could be determined from the energy of activation as defined by Arrhenius with the aid of the quantum hypothesis from the equation

$$E = Nh\nu,$$

where E is the energy of activation, h Planck's constant, and ν the frequency of the activating radiation.

Since the activating frequency must be absorbed by the reacting system, it necessarily follows from this assumption that we can calculate at least one line in the absorption spectrum of a substance undergoing thermal decomposition from the temperature coefficient of that decomposition. It has to be admitted that the experimental proof of this hypothesis is inconclusive. Whilst in some cases the theoretical anticipations have been verified, *e.g.* for the decomposition of triethyl sulphine bromide dissolved in various solvents such as nitrobenzene, where van Halban [4] obtained a value of $E = 28{,}530$ cals. (λ cal. $= 1{\cdot}0\ \mu$), and McC. Lewis and H. A. Taylor [5] observed a strong absorption line at $1{\cdot}05\ \mu$. In the case of the decomposition of phosphine and nitrogen pentoxide the lines anticipated are not observed.[6]

[1] See also *Zeitsch. physikal. Chem.*, 1911, **76**, 129; *Zeitsch. anorg. Chem.*, 1918, **102**, 81; 1919, **106**, 149.

[2] *J. Chem. Soc.*, 1916, **109**, 796.

[3] *Ann. Physik*, 1919, **11**, 5.

[4] *Zeitsch. physikal. Chem.*, 1909, **77**, 129.

[5] *J. Chem. Soc.*, 1922, **121**, 665.

[6] Langmuir, *J. Amer. Chem. Soc.*, **19**, 42, 2190.

Even in those cases in which the anticipated line has been shown to exist, it still remains to be proved that irradiation with light of this frequency will promote photochemical decomposition.

Two other serious criticisms of this presentation of the radiation hypothesis may be advanced. As originally suggested by van t' Hoff and emphasised by Lindemann,[1] unless a light dart or corpuscular nature be attributed to radiation it is difficult to see why all the molecules should not absorb radiation equally and all disintegrate simultaneously; we should thus be confronted with a supposed homogeneous reaction proceeding almost explosively at the surface exposed to radiation. Again, Langmuir has pointed out the great discrepancy between the amount of radiation of the particular wave-length available in a supposed black body enclosure and the actual amount of decomposition effected by it. Langmuir[2] has utilised as his basis of argument the figures for the decomposition of phosphine given by Trautz and Bhandarkar, which are now known to be erroneous. Watson has performed a similar calculation for the decomposition of ethoxyoxalacetic ester, which decomposes according to the unimolecular law.

According to Planck the radiant energy in a black body enclosure encompassed within a band of thickness $\delta\lambda$ is

$$E_\lambda = \frac{2\pi^2 ch}{\lambda^5} \frac{1}{e^{ch/\lambda kT} - 1} d\lambda.$$

In the case of the decomposition of ethoxyoxalacetic ester the energy of activation as calculated from the temperature coefficient of the velocity constant was found to be 35,800 cals., and the absolute velocity constant to be $5{\cdot}37\ 10^{-4}$ at 183° C. Assuming a density of unity the energy required per c.c. per second is

$$\frac{35{,}800 \times 5{\cdot}37\ .\ 10^{-4}}{232} \times 4{\cdot}2\ 10^7 \text{ ergs.} = 3{\cdot}10^6 \text{ ergs.}$$

The wave-length corresponding to the critical increment of 35,800 calories is, according to the Einstein equation, $E = Nh\nu$ and $\nu = \frac{c}{\lambda}$ $\lambda = 800\mu\mu$. Assuming a spectral width for this line of $10\mu\mu$, we obtain $E_\lambda = 2{\cdot}1\ 10^{-7}$ erg./sec. Thus one square centimetre of black body in contact with the ester would supply but an infinitesimal quantity of the actual energy required. This discrepancy between the observed reaction rate and the monochromatic radiation flow has been investigated by Christiansen,[3] and Christiansen and Kramers,[4] in which they show that the maximum rate of activation by radiation per c.c. per second is given by the Einstein expression

$$\frac{\partial N}{\partial t} = N B \rho\nu,$$

[1] *Trans. Farad. Soc.*, 1922, **598**, 17.
[2] *J. Amer. Chem. Soc.*, **42**, 2190.
[3] *Zeitsch. physikal. Chem.*, 1922, **103**, 91.
[4] *Ibid.*, 1923, **104**, 459.

IISc Lib B'lore
541.395 N26
107

where N is the concentration of inactive molecules. $B.\rho r$ is the probability per second that a molecule will become active under the influence of black body radiation of radiation density $\rho\nu$. The rate of reaction is likewise proportional to the number of active molecules or

$$k = A\frac{P_a}{P_n}e^{-\frac{E}{RT}},$$

where P_a and P_n are the *à priori* probabilities of molecules existing in the active and normal states. They find

$$NB\rho\nu = NA\frac{P_a}{P_n}e^{-\frac{E}{RT}}(1 - e^{-E/RT});$$

for large values of E this reduces to

$$NB\rho\nu = NA\frac{P_a}{P_n}e^{-\frac{E}{RT}},$$

and, if P_a/P_n be not very different from unity, the rate becomes

$$k = Ae^{-\frac{E}{RT}} = B\rho\nu,$$

where $\frac{1}{A}$ is the life of an excited molecule. This is assessed as equal to 10^{-8} seconds.

Tolman [1] has attempted to evaluate B from the Bohr correspondence principle by means of the expression

$$B = \frac{2\pi^3e^2}{3h^2}E^2,$$

leading to values of B from 10^{14} to 10^{19}. Hence an upper limit is found for $k = 10^{20}\rho\nu$, and evaluating $\rho\nu = \frac{8\pi h\nu^3}{C^3}e^{E/RT} - 1$ (or approximately $\frac{8\pi h\nu^3}{C^3}e^{-\frac{E}{RT}}$) we obtain $k = Ca.10^7e^{-\frac{E}{RT}}$ for $E = 25{,}000$ calories.

Now the rate of a number of supposedly unimolecular reactions [2] is of the order of $10^{14}e^{-\frac{E}{RT}}$, whence a rate of $10^8e^{-\frac{E}{RT}}$, which is the maximum rate possible for activation by black body radiation, is only one-millionth of the observed values. Several attempts have been made to avoid this difficulty. Perrin [3] suggests that the light quantum is re-emitted after decomposition of the active molecule and passes on to the next. If this hypothesis were true it is difficult to see why the same phenomenon does not occur in true photochemical reactions where a number of cases of the Einstein law of photo-equivalence have been found. Tolman [4] and Rideal [5] assume that the whole of the

[1] *J. Amer. Chem. Soc.*, 1925, **47**, 1543; *Phys. Rev.*, 1924, 23643.
[2] Dushman, *J. Amer. Chem. Soc.*, 1921, **43**, 397.
[3] *Trans. Farad. Soc.*, 1922, **17**, 605.
[4] *J. Amer. Chem. Soc.*, 1920, **42**, 2506; 1925, **17**, 1526.
[5] *Trans. Farad. Soc.*, 1922, **17**, 605.

inflowing radiation is available for activation. Such an operation can be imagined to proceed by considering the activation of molecules to take place in steps, by absorption of smaller quanta, there being a number of stages corresponding to a number of absorption lines in the spectrum of the substance. This conception, together with the assumption that absorption of the energy in a particular part of the spectrum is accompanied by a rapid redistribution of energy so as to give the typical black body energy wave-length curve, accounts, as Tolman has shown, for the existence of a temperature coefficient of photochemical actions. We may note, for example, in the case of the decomposition of oxalacetic ester at 18·3° the energy necessary for activation was found to be $3{\cdot}0\ 10^6$ ergs per c.c. per second, whilst the total energy in a black body enclosure per cubic centimetre is given by Stefan's equation

$$E = 3{\cdot}72\ 10^{-5}T^4 \text{ or } 2{\cdot}4\ 10^6 \text{ ergs. at } 183° \text{ C.}$$

This view, in a slightly different form, has been advanced by G. N. Lewis and Smith,[1] who have calculated on the hypothesis of discrete quanta of cross-sectional area $A = \frac{\lambda^2}{8\pi^2}$,[2] the probability of collision between molecules and quanta, the former possessing a certain internal energy e, and the latter of frequency ν, such that $e + h\nu' = \epsilon_e$.

The chance ϕ' that a molecule will encounter a quantum moving with the velocity of light c of any frequency above a given frequency ν' is found to be

$$\phi' = \int_{\nu'}^{L} A \quad c\frac{\partial\rho}{\partial\nu}\delta\nu,$$

where

$$\frac{\partial\rho}{\partial\nu} = \frac{\rho\nu}{h\nu} = \frac{8\pi\nu^2}{c^3}e^{-\frac{h\nu}{kT}},$$

whence

$$\phi' = \frac{kT}{h}e^{-\frac{h\nu'}{kT}}.$$

The chance that a molecule possessing internal energy e will encounter a quantum of frequency higher than ν' in unit time will be

$$d\rho = \phi'\frac{dw}{de}de,$$

where $\frac{dw}{de}$ is the fraction of molecules having internal energy between e and $e+de$.

Hence the chance P that a molecule chosen at random will in unit time meet a quantum which has sufficient energy to take the molecule from the unactivated to the activated state.

$$\rho = \int_{E}^{E_c}\phi\frac{dw}{de}de = \frac{kT}{Eh}\int e^{-\frac{E-E_c}{RT}}\cdot\frac{dw}{de}de,$$

[1] *J. Amer. Chem. Soc.*, 1925, **47**, 1519. [2] See also Rideal, *Phil. Mag.*, 1920, **40**, 463.

where e is the internal energy of the molecule and e_c the critical value. In a molecular system possessing no internal energy except that of rotation with two degrees of freedom we obtain

$$\frac{dw}{de} = \frac{1}{kT} e^{-\frac{E}{kT}},$$

whence

$$\rho = \frac{E_c}{h} e^{-\frac{E_c}{kT}},$$

an equation originally suggested by Dushman and Rideal.

A similar equation can be developed for molecules possessing more than two degrees of freedom.

It will be noted that these modifications of the original hypothesis are in essentials somewhat similar, in that a part of the necessary critical energy increment is already present as internal energy in a molecule undergoing activation; whilst Tolman would suggest that all internal energy is supplied by radiation, G. N. Lewis merely postulates its existence and sees in this a part of the energy necessary for activation.

On the redistribution of internal energy as a mechanism of activation.—In the preceding section we have examined the various attempts which have been made to reconcile the experimental rates of reaction with the hypothesis that the energy of activation is supplied by the inflow of black body radiation. The outcome can scarcely be regarded as satisfactory, and in consequence many have rejected the radiation theory *in toto* and have fallen back on the theory of activation by collision, which we shall have occasion to discuss in the next section. Before this attitude can be justified it is clearly necessary to show that there are no unimolecular chemical reactions, because, although the original conception of Perrin, Trautz, and McC. Lewis that the inflowing radiation was the source of activation may be erroneous, the very existence of a true unimolecular reaction certainly demands an explanation in terms of some type of interaction between radiation and matter.

The only definite example of a well-established case of unimolecular decomposition is that of nitrogen pentoxide, although many cases of evaporation and sublimation,[1] and, within certain limited temperature ranges, the thermal decomposition of sulphuryl chloride,[2] likewise conform to a reaction rate of the first order.

The decomposition of nitrogen pentoxide has been the subject of numerous investigations by Daniels and his co-workers,[3] Lueck,[4] White and Tolman,[5] Hirst,[6] and Hirst and Rideal.[7] It is found that from

[1] Rideal, *Proc. Camb. Phil. Soc.*, 1921, **26**, 241.
[2] Smith, *J. Amer. Chem. Soc.*, 1925, **47**, 1862.
[3] *J. Amer. Chem. Soc.*, 1921, **43**, 53; *ibid.*, 1922, **44**, 2402; *ibid.*, 1925, **47**, 1602.
[4] *Ibid.*, 1922, **44**, 757.
[5] *Ibid.*, 1925, **47**, 1240.
[6] *J. Chem. Soc.*, 1925, **127**, 657.
[7] *Proc. Roy. Soc.*, 1925, **109A**, 526.

high pressures down to *ca.* 0·25 mm. the reaction velocity may be expressed in the form

$$-\frac{dc}{dt}=4{\cdot}98\,.\,10^{13}e^{-\frac{24{,}700}{RT}}c,$$

viz. the mean value determined from the data of Daniels and Hirst; below 0·25 mm. the reaction velocity increases to a limiting value at considerably smaller pressures where the reaction rate is a little over five times that at high pressures, or

$$-\frac{dc}{dt}=2{\cdot}53\,.\,10^{14}e^{-\frac{24{,}700}{RT}}c,$$

a value in close agreement with that given by the equation of Dushman [1] and Rideal,[2]

$$-\frac{dc}{dt}=\nu e^{-\frac{Nh\nu}{RT}}c=2{\cdot}59\,.\,10^{14}e^{-\frac{24{,}700}{RT}}c.$$

Between the pressures of 0·25 mm. and the smaller values the reaction velocity constant increases, and it was shown by Hirst and Rideal that the experimental data were in agreement with the hypothesis that, of the total number of active molecules present at any time, viz. $Ne^{-\frac{Nh\nu}{RT}}$, one-fifth of them decomposed at once, but four-fifths of them had to remain in the active state without suffering deactivating collision for $9{\cdot}5\,.\,10^{-7}$ seconds before decomposition occurred, the velocity of decomposition being expressible in the form

$$-\frac{dc}{dt}=4{\cdot}98\,.\,10^{13}\left\{1+4{\cdot}09e^{-1{\cdot}003P}\right\}e^{-\frac{24{,}700}{RT}}c,$$

where P is the pressure in millimetres and $e^{-1{\cdot}003P}$ the fraction of the active molecules having a life of $9{\cdot}5\,.\,10^{-7}$ seconds.[3] The possibility of the energy of activation being resident in any one of the five NO groups of the N_2O_5 molecule, and of decomposition only taking place on activation of one particular group, the time necessary for the energy to leave one $-NO$ group and enter the particular group being $9{\cdot}5\,.\,10^{-7}$ seconds, immediately suggest themselves as a plausible explanation why some molecules require a "life" before decomposition. It is clear that the decomposition of nitrogen pentoxide is unimolecular in character down to pressures so low that explanations on the hypothesis of activation by any form of molecular impact are not very probable. At the same time the inflowing radiation is inadequate to provide the necessary energy.

We may note that, if the decomposing gas were confined in a radiation impermeable envelope, at any moment the rate of decomposition of molecules with the concomitant liberation of internal energy

[1] *J. Amer. Chem. Soc.*, 1921, **43**, 397. [2] *Phil. Mag.*, 1920, **40**, 461.
[3] Cf. Jeans, *Dynamical Theory of Gases*, p. 258.

of activation would be equal to the rate of formation of new active molecules, this rate of decomposition and formation being given by the equation referred to above. Thus, no supply of new energy of activation is required, merely a redistribution of internal energy amongst the molecules.

In the particular degree of freedom, comprising one of the oscillators in the molecule, which, on activation, causes molecular disruption, there is at any temperature, on the average, RT calories. This average value, however, is not the result of equal distribution amongst all the molecules, but the various molecules differ from one another in the possession of different numbers of quanta, those possessing such a number that the energy content in this degree of freedom is $Nh\nu$ or 24,700 calories per grm.-mol. are said to be activated. We may logically infer that the energy of activation is already present inside the molecules as internal energy, being originally supplied by infra-elastic collision, a method which we shall discuss in the next section. We must therefore examine the various methods by which the distribution of this internal energy can be effected amongst the various molecules. It is clear that the usual method of redistribution by molecular collision is much too slow to effect activation at the necessary rate; some type of "quantum sprung" postulated by Polanyi[1] is clearly necessary, but the mechanism by which a quantum liberated by a decomposing molecule is absorbed by another is by no means clear.

The data of Warburg and Leithauser[2] show a number of absorption bands for nitrogen pentoxide between 2·4 and 8·7μ, with a particularly strong line at 5·81 which is five times that calculated from the critical energy movement, viz. 1·16μ; the possibility of the redistribution of the energy of the internal specific heat by the emission and absorption of quanta of small size is thus not negatived by spectroscopic evidence. Two difficulties, however, have to be overcome in this conception. If we imagine a molecule possessing, say, two quanta, it is evident that this molecule can either receive another or loose one, it may in fact become a creditor or debtor molecule. The conditions under which a molecule may become a creditor or debtor must be governed by some type of fluctuation not connected with molecular impact; it is possible that the radiation flowing in the system may render molecules oscillating in phase with it creditors and those out of phase debtors. Again, on the assumption of the passage of quanta from molecule to molecule it is necessary that the absorption coefficient be extraordinarily large, for the inflowing and eflowing radiation of these wave-lengths is but a very small fraction of the number of quanta flowing from molecule to molecule within the system. The absorption coefficient in those cases must be much larger than those experimentally

[1] *Zeitsch. f. Physik*, 1920, I. 337; *ibid.*, 1920, II. 90; 1920, III. 31.
[2] *Ann. Physik*, 1909, **28**, 313.

bserved for fluorescent radiation, and we are led to the conception
f the interlinkage (in the manner suggested by Sir J. J. Thomson)
f the moving molecules with one another by Faraday tubes along
hich the quanta flow. It is generally assumed that the quantum
oss-sectional area grows with the wave-length ($A\alpha\lambda^2$); thus, the
olume of space swept out by a quantum in its motion increases
pidly as we proceed into the infra-red portion of the spectrum; the
pportunity of collision with molecules is thus enhanced. Since the
ave-length 5·81μ is some twenty times that of the resonance line
mercury vapour (2540 A°), the opportunity of collision with molecules
nd thus the coefficient of absorption will on this view be some four
undred times greater. On analogy with the case cited by Lewis and
mith,[1] the lowest pressure at which the decomposition of N_2O_5 has
een examined is 0·05 mm., which is about one hundred times greater
an the pressure at which Wood examined the absorption of the line
540 A° by mercury vapour. A 50 per cent absorption would take
ace in a layer of *ca.* 0·05 mm. if the coefficient of absorption were
qually great as for mercury vapour. If the coefficient is four hundred
mes greater it is clear that virtually complete absorption of the
diation continually emitted by the molecules in the gas will occur.

The theory of activation by collision.—We have noted the simple
diation theory of chemical action is certainly not tenable, and that
any drastic amplifications are required before this attractive con-
ption can be made reconcilable with experimental data. The
mewhat arbitrary hypotheses necessary for this purpose have led
any to reject *in toto* the conception of activation by radiation and
inquire how far it is possible to assume activation by collision.
ccording to this view, when molecules impinging on one another
th such initial speeds that the available energy in the case of a
mple bimolecular reaction between molecules of mass m exceeds
e critical energy increment, or

$$\tfrac{1}{4}mV^2 > E_C,$$

ey do not suffer elastic collision but undergo activation and dis-
ption.[2] The data of Hinshelwood and Pritchard, on the bimolecular
composition of chlorine monoxide,[3] of nitrous oxide,[4] and of
odenstein on hydrogen iodide,[5] strongly support this view.

Thus, in the case of nitrous oxide decomposition, the rate is found
be expressible between the temperature range 838° K to 1125° K
means of the following equations:

$$-\frac{dc}{dt} = Kc^2 \qquad K = 7{\cdot}60 \,.\, 10^{12}\sqrt{T}\; e^{-\frac{58{,}450}{RT}},$$

[1] *Loc. cit.* [2] Lindemann, *Trans. Farad. Soc.*, 1922, **17**, 598.
[3] *J. Chem. Soc.*, 1923, **123**, 2730.
[4] Hinshelwood and Burk, *Proc. Roy. Soc.*, 1924, **106A**, 284.
[5] Bodenstein, *Zeitsch. physikal. Chem.*, 1924, **124**, 233.

where 58,480 cals. is the energy of activation per two grm.-mols. of the gas. The rate of activation by collision is given by the kinetic theory

$$\frac{dA_c}{dt} = Nc^2\sigma^2\sqrt{\frac{4\pi RT}{17}}\, e^{-\frac{E}{RT}},$$

where σ is the molecular diameter.

If we adopt a value of $\sigma = 3{\cdot}32 \,.\, 10^{-8}$ cm. we obtain for the rate of activation by collision

$$\frac{dA_c}{dt} = c^2 3{\cdot}25 \,.\, 10^{12}\sqrt{T}\, e^{-\frac{58,450}{RT}};$$

since two molecules disappear as the result of each such collision the rate of decomposition is clearly

$$-\frac{dc}{dt} = 6{\cdot}50 \,.\, 10^{12}\sqrt{T}\, e^{-\frac{58,450}{RT}} c^2,$$

a value so close to that experimentally obtained that there can be little doubt that this hypothesis does provide an adequate explanation for the mechanism of bimolecular reactions, and that no other means of activation is required.

If infra-elastic collisions take place, it is necessary also that supra-elastic collisions occur at the same time; thus, if we imagine molecules becoming activated by the conversion of kinetic energy lost on impact into eternal energy in the quantised form, we must at the same time postulate the contact of an activated molecule with a normal molecule resulting in the reliberation of the internal energy in the kinetic form (a collision of the third kind, to continue the somewhat unsatisfactory classification of collision types). Thus, if the average kinetic energy of each molecule before collision be e and one molecule possess internal energy of activation e^x, the average kinetic energy after collision will be e' such that

$$2e' = 2e + e^x.$$

Whilst the existence of infra-elastic and supra-elastic collisions have been well established in a number of cases of electron-molecule impacts, the experiments on activation by molecular collision, which is the basis of this mechanism of chemical change, are more limited. Franck and his co-workers [1] have demonstrated the transfer of internal energy from one molecule to chemical energy in another by effecting the dissociation of hydrogen molecules ($E = 90{,}000$ cals.) with the aid of excited mercury atoms. They have also shown that, at 300° C., excited mercury atoms will, when mixed with thallium vapour, cause the emission of the characteristic thallium line, corresponding to an excitation of 6·1 volts. Since the excited atom is only at a level

[1] Cario, *Zeitsch. f. Physik*, 1922, **9**, 259; 1922, **12**, 162.

rresponding to 5·8 volts it is clear that an additional supply of ternal energy equivalent to 0·3 volt (1 volt fall is equivalent to ,900 calories) must have been supplied by the infra-elastic collision etween an excited mercury atom and a normal thallium atom.

Reaction chains and the concept of hot molecules.—In many notochemical actions the Einstein law of photoequivalence is not beyed, and a ready interpretation of many of these was given by ernst. According to Nernst, the photochemical combination of ydrogen and chlorine consists in the primary photochemical formation chlorine and hydrogen atoms from their respective molecules, and is in turn is followed by a series of reactions such as

$$Cl + H_2 = HCl + H,$$
$$H + Cl_2 = HCl + Cl.$$

here is some evidence, due to Norrish, that such atom chains may mmence on the walls of the reaction vessel and proceed through the s phase until they strike the wall again. Both chlorine atoms and ydrogen atoms are immobilised on the walls and may there react ith atoms of like or opposite kind. We shall have occasion to discuss e action of the mechanism and the influence of catalysts on these actions in more detail in a later section.

Christiansen and Kramers [1] have attempted to extend this conception systems in which *atom* chains are not possible. According to their ew, the product of decomposition of a molecule after excitation must ossess in itself the original energy of excitation and either an addition a diminution equal to the heat of reaction. If the reaction be othermic of value q per molecule the total energy of the product ll be

$$h\nu + \tfrac{1}{2}mv^2 + q,$$

here $h\nu$ is the energy of activation, v the molecular velocity, and q e heat of reaction.

The molecules thus possess much more energy than their neighbours; e authors do not commit themselves as to how this energy is stored these fresh products of reaction, but it would appear that they visage the probability of "hot" molecules or the energy is in the netic form. These "hot" molecules can, by impact, activate by llision of the second kind another reactant molecule, and thus give se to reaction chains.

The presence of inert gases is frequently without influence on e reaction rate and reactions may also proceed in solution, *e.g.* the composition of hydrogen peroxide or nitrogen pentoxide; thus, the pothesis of kinetically "hot" molecules would appear to be excluded. gain, the view that the energy, if internal, can only be handed on to reactant and not to a diluent or solvent molecule, assumes that a bration frequency is common to both reactant and product, an

[1] *Loc. cit.*

assumption that still awaits experimental verification. The suggestion, however, is not without interest, for such a mechanism has been shown by Watson in the following manner to give rise to pseudo-unimolecular constants.

Arrhenius has expressed the opinion that there is a dynamic equilibrium between the inactive and active molecules, the latter existing in but small quantities. We may consequently write

$$C_a = \alpha C_n, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where C_a is the concentration of active molecules,
C_n those of the inactive molecules,
α a small factor.

If the active product molecules are the main factor in activation then the concentration of active molecules will be determined by the product of normal molecules C_n and the number of such activating molecules C_a', or

$$C_a = \alpha' C_n C_a'. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The query then arises, Under what conditions are these two equations compatible with a unimolecular reaction defined by the expression

$$k = -\frac{1}{C_n}\frac{dC_n}{dt}?$$

We may represent our reacting system diagrammatically as follows:

$$n \rightleftarrows a \longrightarrow a',$$

the first reversible expression representing the Arrhenius equilibrium between normal and active molecules, the second the irreversible decomposition of the active molecules, which is assumed to take place sufficiently slowly as not to effect the equilibrium $n \rightleftarrows a$.

The rate of decrease of the normal molecules must be equal to the rate of increase of the active molecules plus the rate of spontaneous decomposition of the a molecules into the products a',

or
$$-\frac{dC_n}{dt} = \frac{dC_a}{dt} + SC_a, \quad . \quad . \quad . \quad . \quad (3)$$

where $\frac{1}{S}$ is the mean life of an active molecule.

From (1)
$$\frac{dC_a}{dt} = \alpha\frac{dC_n}{dt};$$

$$\therefore -\frac{dC_n}{dt} = \alpha\frac{dC_n}{dt} + S\alpha C_n,$$

i.e.
$$-\frac{dC_n}{dt}(1+\alpha) = S\alpha C_n.$$

$$-\frac{1}{C_n}\frac{dC_n}{dt} = \frac{S\alpha}{1+\alpha} = \text{a constant at constant temperature.} \quad . \quad (4)$$

We have already noted that Marcelin showed that the ratio

$$\frac{C_a}{C_n} = e^{-\frac{E}{RT}}.$$

his expression has been modified by Einstein [1] to the form

$$\frac{C_a}{C_n} = \frac{P_a}{P_n} e^{-\frac{E}{RT}},$$

here P_a, P_n are the *à priori* probabilities of the molecule existing in ie active or normal state. In general $P_a = P_n$. Similar considerations old when the " normal " state is also active (a''), or

$$\frac{C_a}{C_{a''}} = \frac{P_a}{P_{a''}} e^{-\frac{(E-E'')}{RT}},$$

here E and E'' are the energies of activation in each state.

Replacing this value of $\frac{C_a}{C_n} = \alpha$ in (4),

$$-\frac{1}{C_n}\frac{dC_n}{dt} = \frac{Se^{-\frac{E}{RT}}}{1+e^{-\frac{E}{RT}}} = Se^{-\frac{E}{RT}}, \quad . \quad . \quad . \quad (5)$$

nce α is small by hypothesis ; and we thus obtain our original equation hich we have already noted as applicable to unimolecular reactions.

From Equation (4) we may evidently obtain the ratio of active to active molecules in the Arrhenius equilibrium mixture from a nowledge of k and s. For the decomposition of nitrogen pentoxide $=487 \cdot 10^{-3}$ and $s = 10^{-14}$ or α the ratio is *ca.* 10^{-17}.

Such a mechanism as has been postulated by Christiansen and ramers leads to the general expression of a unimolecular reaction in nich S is now accurately defined as the probability that an active olecule will decompose within the next second, *i.e.* $\frac{1}{S}$ is the average life.

It has been assumed for this purpose that the active molecule at e moment of decomposition or just after decomposition hands on s energy to activate a new molecule. It is possible that the products decomposition which are active at the moment of production may, fore they relapse into the normal products, likewise impart their ergy by collision and thus give rise to reaction chains. Watson s obtained in the following manner the conditions that the reaction ould be unimolecular.

There are two possible cases which may be represented diagrammatic-y as follows :

(1) $n \rightleftarrows a \longrightarrow a' \rightleftarrows n'$.

(2) $n \rightleftarrows a \longrightarrow a' \longrightarrow n'$.

[1] *Physikal. Zeitsch.*, 1917, **18**, 121.

INDIAN INSTITUTE OF SCIENCE LIBRARY

The problem is to find under what conditions this will be a constant. If the change $a \longrightarrow a'$ is much quicker than from $a' \longrightarrow n'$ then $\frac{C_a}{C_{n'}}$ and therefore $\alpha' C_n$ will be small in comparison with unity, and we know already that $\alpha' C_{a'} = \frac{C_a}{C_n}$ is small compared with unity.

Hence $$K = -\frac{1}{C_n}\frac{dC_n}{dt} = \alpha' C_{a'}(S - S') = \alpha' C_{a'} S,$$

since S is much greater than s in the above assumption.

The a molecules are in the same position as a radioactive element, and therefore when the reaction is proceeding steadily C_a is constant and the reaction will be unimolecular again; however, by (2), this leads to the existence of an Arrhenius mass equilibrium between active and inactive molecules, or $\frac{C_a}{C_n} = \alpha' C_{a'} = \text{Constant}$.

In that case we have assumed that the change $a' \longrightarrow n'$ is slower than the change $a \longrightarrow a'$, which in turn is already assumed much slower than the change $n \longrightarrow a$ or $a \longrightarrow n$, or the deactivation of the active product is required to be very much slower than the deactivation of the active reactant. Such conditions are evidently fulfilled, according to Tolman's calculations,[1] when the energy of activation of the reactant is much larger than the energy of activation of the product.

Watson has summarised the conclusions drawn from this development of the hypothesis of Christiansen and Kramers as follows:

(1) If the energy of activation be acquired from highly energised reaction products the reaction will be unimolecular in type only if there exists a simple proportionality between the concentration of active and inactive molecules, as postulated by Arrhenius.

(2) If the deactivation of the active products takes place reversibly the reaction will be, in general, autocatalytic.

(3) If the deactivation be spontaneous and irreversible, the law will be that of a unimolecular reaction provided that the deactivation is much slower than the loss of energy by the active resultant.

It must be admitted that this attractive conception of chain mechanism still awaits exact experimental confirmation.

Active molecules.—Although the arguments are by no means conclusive, there are strong reasons for assuming that the active molecules postulated by Arrhenius are identical with the "excited" molecules of the physicist. The distortion of the molecule or the quantity of energy required to send the electron to its new orbit is, for most chemical processes, much smaller than those which have been made the subject of experimental physical research; for, in general, the wave-length of the equivalent quantum of energy is confined to

[1] *Loc. cit.*

the infra-red portion of the spectrum. Further, we must assume that molecular excitation may be produced not only by the usual methods of absorption of radiation or by collision with α-particles or electrons, but also by molecular collision.

The lives of excited molecules.—Experimental determinations of the time of emission of radiation have been made by Wien [1] and Dempster,[2] and periods have been calculated by Milne,[3] Stern and Vollmer,[4] Turner [5] and Tolman,[6] Saha,[7] Weigert and Kellermann.[8] The following observed and calculated values are obtained:

	Experimental.	Calculated.	
Hg	$1{\cdot}03 \cdot 10^{-7}$ sec. I_2	($\lambda = 5461$)	$2{\cdot}94 \cdot 10^{-3}$ sec.
Hβ	$5{\cdot}0 \cdot 10^{-8}$ „ HCl	($\lambda = 32340$)	0·0174 sec.
Hα	$2{\cdot}0 \cdot 10^{-8}$ „ HCl	($\lambda = 34150$)	0·829 sec.

The experimental values for τ for excitation in visible light are all of the order of 10^{-7} seconds, whilst those calculated on the correspondence principle increase very rapidly as the energy of the quantum decreases; this increase has not, however, yet received any experimental confirmation. Since, in the majority of chemical actions, the energies of activation involved are relatively small, it is a matter of great importance to find out whether the long lives anticipated by Tolman for molecules activated by collisions of the second kind do actually exist.

The original experimental equation of Arrhenius may be integrated in the following form:

$$\log_e K = -\frac{E}{RT} + C$$

or

$$K = e^C e^{-\frac{E}{RT}}.$$

If C be the integration constant, e^C may be replaced by S where $C = \log_e S$, whence

$$K = Se^{-\frac{E}{RT}}.$$

It is clear that if the term $e^{-\frac{E}{RT}}$ represents the fraction of excited or active molecules, S has consequently the dimensions of a frequency, and is regarded by many as the reciprocal of the time (τ) necessary for the molecule to pass from the active or excited to the inactive or passive condition.

Others have suggested [9] that this time is not the time required for the emission of its internal energy as radiation but represents rather the average time before a crisis occurs in the active molecule. At this crisis the molecule either undergoes chemical reaction or commences to revert to the normal form. These crises are possibly connected

[1] *Ann. Physik*, 1919, **60**, 597; 1921, **66**, 229.
[2] *Phys. Rev.*, 1920, **15**, 158.
[3] *Proc. Camb. Phil. Soc.*, 1925, **22**, 493.
[4] *Physikal. Zeitsch.*, 1919, **20**, 183.
[5] *Phys. Rev.*, 1924, **2**, **23**, 464.
[6] *Ibid.*, 1924, **23**, 693.
[7] *Phil. Mag.*, 1924, **6**, **48**, 421.
[8] *Zeitsch. physikal. Chem.*, 1923, **107**, 1.
[9] Dushman, *J. Franklin Inst.*, 1920, **189**, 515; *J. Amer. Chem. Soc.*, 1921, **43**, 403; Rideal, *Phil. Mag.*, 1920, **40**, 462.

with the position of the electron in its unstable orbit; since its frequency is given by the expression $E = Nh\nu$, we obtain $S = \nu$ or $K = ve^{-\frac{E}{RT}}$. Amongst other suggestions it has been proposed that $\frac{1}{S}$ represents a time period $\frac{1}{\nu'}$ where ν' is a frequency of the molecule, but not necessarily that derived from the temperature coefficient.[1] It may be noted in passing that 10^{-14} seconds, which is of the same order as ν for ultra-violet frequencies, is also the computed period of the duration of an elastic collision.

The energies of activation in the presence of catalysts.—A number of cases have been examined on the alteration of the velocity constant as well as of the temperature coefficient of a chemical reaction when either reacting molecule possesses different substituent groups or various solvents are employed. Whilst the reactions are undoubtedly complex and deductions based on an assumed simplicity are open to criticism, nevertheless some interesting relationships have been obtained.

Nicoll and Cain [2] have examined the rate of decomposition of the substituted diazobenzene chlorides in excess of water according to the reaction

$$RC_6H_4N_2Cl + H_2O \longrightarrow RC_6H_4OH + N_2HCl.$$

The reaction is pseudo-unimolecular and can be expressed in the form

$$-\frac{1}{x}\frac{dx}{dt} = Se^{-\frac{E}{RT}}.$$

That a formal relationship between S and E exists has been pointed out by Watson and is evident from the following data :

Substituent group R.	E cals. per grm.-mol.	$\text{Log}_{10} S$.	$\frac{E}{\text{log}_{10} S}$
H	24,300	13·6	1790
o.-CH_3	25,100	14·6	1720
m.-CH_3	22,900	13·0	1760
p.-CH_3	27,900	15·0	1860
p.-SO_3H	28,200	14·9	1890
m.-NO_2	30,500	15·0	2030

The value of E likewise changes in the case of the substituted oxalacetic esters (EtOOC – CO – CHR . COOEt) examined by Watson, which undergo decomposition in a pseudo-unimolecular manner :

[1] Christiansen, *Zeitsch. physikal. Chem.*, 1922, **103**, 91.
[2] *J. Chem. Soc.*, 1903, **83**, 470.

Substituent group R.	E cals. per grm.-mol.	$\text{Log}_{10} S$.	$\frac{E}{\log_{10} S}$
$-OC_2H_5$	33,800	13·94	257
$-CH_3$	33,300	13·36	249
$-CH_2COOC_2H_5$	35,400	14·30	247
$-C_6H_5$	44,300	19·88	223

Alterations in E may likewise be produced when, instead of altering the molecular structure of the reactant, we change the solvent, the influence of which we shall discuss in a subsequent section. The following data, calculated from Cox, on the addition of aniline to bromacetophenone,[1] may be cited in this connection:

Solvent.	E cals.	K 37·8° C.
C_6H_6	8,088	·000985
CCl_3H	10,760	·00186
$C_6H_5NO_2$	13,470	·0135
CH_3COCH_3	11,080	·0764
$C_6H_5CH_2OH$	14,290	·0440
N. butyl alcohol	14,060	·0550
Ethyl alcohol	13,910	·0626
Methyl alcohol	12,440	·0748

Similar alterations of the critical increment with the solvent may be noted in the data of von Halban[2] for triethyl sulphine bromide, and of Dimroth[3] on the decomposition of the methyl ester of benzyl 5, hydroxy 123, triazole benzoate.

Decomposition of Triethyl Sulphine Bromide.		Decomposition of the Triazole Benzoate.	
Solvent.	E cals.	Solvent.	E cals.
Nitrobenzene	28,330	Acetone	29,140
Tetrachlorethane	30,390	Ethyl alcohol	30,640
Iso-amyl alcohol	33,190	Chloroform	35,420
N. propyl alcohol	33,750		
Benzyl alcohol	75,920		

We note that the energies of activation are definitely affected by solvents; it is for this reason that the theoretical considerations advanced in the preceding paragraphs are of importance in the study of catalytic reactions both homogeneous and heterogeneous. Evidence is slowly accumulating that it is to the catalytic agent that we must turn if it is desired to reduce the energy increment necessary to produce

[1] *J. Chem. Soc.*, 1921, **119**, 142. [2] *Loc. cit.* [3] *Lieb. Ann.* **373**, 336, 1410.

a certain reaction process. In all probability the initial process in the catalysis is a deformation of the structure of the molecule by association with the catalytic agent, either as a molecular complex or compound in homogeneous catalysis or as an adsorbed atom or molecule on a contact catalyst. That such association materially alters the energy required for reaction to occur is to be concluded from recent studies in the domain of photochemistry, and especially in the hydrogen-chlorine combination. An examination, by Coehn and his co-workers,[1] of the insensitivity of dry hydrogen-chlorine mixtures to visible light has indicated such a conclusion. They have shown that whereas moist mixtures of these two gases are photo-sensitive in the blue region of the spectrum, the gas mixtures in which the water-vapour pressure is of the order of 10^{-7} mm. are first sensitive in the ultra-violet region below $\lambda = 3000$ A°. The energy quantities involved are respectively about 52,500 cals. in the water catalysed reaction and 94,500 cals. in the non-catalysed reaction.

Homogeneous reactions in solutions.—The considerations advanced in the preceding sections may be applied to the more complicated cases of liquids. We have noted that unimolecular reactions in gaseous systems are extremely rare and must conclude that the same is true in solution; thus, cases of dynamic isomerism, *e.g.* acetoacetic ester, cannot be satisfactorily explained on the hypothesis of an intra-molecular reaction, although this view is still maintained by some investigators. In solutions, also, complexes or solvates may be formed; the study of bimolecular reactions in gases indicates a possibility that the reaction of tautomeric change may take place through activation by collision between solvent and solute molecule, but, as we shall note, the critical energy increment is high and the reaction velocity negligible at ordinary temperatures. It is for this reason that it is probable that most reactions in solution occur through the intermediary of ternary complexes, reactant, solvent, catalyst. In order to justify this point of view, we must determine the evidence in favour both of the existence of such complexes and also why such complexes are more easily activated and thus undergo reaction more readily than the simpler binary constituents also present in the system.

To obtain some idea of the mechanism of such reactions we must examine both the form of the reaction velocity concentration relationships and the influence of temperature on the velocity coefficient. It is found in the majority of cases that a reaction proceeding in dilute solutions according to the equation

$$a + b \longrightarrow d$$

proceeds at a velocity that is proportional to the bulk concentrations,

$$\frac{dx}{dt} = k(a)(b).$$

[1] *Ber.*, 1923, **56**, 458, 696; *Zeitsch. physikal. Chem.*, 1923, **105**, 356; 1924, **110**, 705.

n more concentrated solutions this equation fails. Whilst Arrhenius, stwald, and Euler noted a parallelism between the reaction velocity nd the osmotic pressure of the reactant, the more precise conception f thermodynamic concentration introduced by G. N. Lewis has, of ter years, been applied to reaction velocities by Harned [1] and cC. Lewis,[2] who suggested that, in lieu of concentrations, the tivities or thermodynamic concentrations of the reactants should e employed. The equation then becomes

$$\frac{dx}{dt} = k(a)(b)f_a f_b,$$

here $f_a f_b$ are the activity coefficients of the reactants.

Brönsted [3] assumed that the reaction would proceed by the rmation of an unstable intermediate complex (ab) which underwent pid decomposition to the products c or $a + b \xrightarrow{\text{slow}} (ab) \xrightarrow{\text{fast}} c$.

The assumption that the velocity of reaction was determined by e ratio of the activities of the reactants to that of the products ads to the equation

$$\frac{dx}{dt} = k_1(a)(b)\frac{f_a f_b}{f_c}.$$

Bjerrum has criticised this equation [4] from two points of view. hilst the insertion of activities in lieu of actual concentrations may justifiable in systems at, or close to, equilibrium, it is probably roneous to assume that the number of collisions in a system under- ing reaction is influenced by the activities, although the number effective collisions may be determined by the factor. Again, the te at which the complex (ab) undergoes reaction is not demonstrably fluenced by its potential; thus, in radioactive transformation the te of decay is uninfluenced by the activity of the system.

Bjerrum assumes that the reaction velocity is proportional to the ncentration of the complex ab, or

$$\frac{dx}{dt} = k(ab).$$

cording to the law of mass we obtain

$$\frac{(a)(b)}{(ab)}\,\frac{f_a f_b}{f_{(ab)}} = K,$$

here K is the mass action equilibrium constant.

ence

$$\frac{dx}{dt} = k'\frac{(a)(b)f_a f_b}{f_{(ab)}}.$$

[1] *J. Amer. Chem. Soc.*, 1918, **40**, 1461.
[2] *J. Chem. Soc.*, 1920, **117**, 1120; 1922, **121**, 1613.
[3] *Zeitsch. physikal. Chem.*, 1922, **102**, 169.
[4] *Ibid.*, 1923, **108**, 85.

On this view the reaction velocity is defined by two terms, the concentration and the stability of a complex. The existence of such complexes in solution, *e.g.* of esters and acids, sugars and water, has been fully demonstrated by the work of Kendall and his co-workers.

The action of catalytic agents in accelerating the reaction velocity of a typical homogeneous reaction is due to the formation of a new complex present in different amount and of different stability to the original. Thus, in the above reaction, if a catalyst of concentration c be added, the reaction velocity will be expressed by the equation

$$\frac{dx}{dt} = k' \frac{(a)(b) f_a f_b}{f_{ab}} + k'' \frac{(a)(b)(c) f_a f_b f_c}{f_{(abc)}}.$$

Whether any reaction proceeds in the absence of a catalytic agent, *e.g.* the mutarotation of sugars or the isomeric change of nitro-camphor or aceto-acetic ester,[1] cannot, of course, be verified experimentally, as results either positive or negative are evidently susceptible to criticism. An examination of the temperature coefficient of catalysed reactions, however, leads one to infer that many reactions virtually do not proceed at all in the absence of catalysts.

The extremes of the temperature coefficients of such catalysed reactions are found to be $\frac{K_{35}}{K_{25}} = 4{\cdot}13$ for the hydrolysis of cane sugar in the presence of hydrochloric acid, and 1·82 for the hydrolysis of methyl acetate in the presence of caustic soda, corresponding to energies of activation of 26,000 and 10,900 cals. per grm.-mol. respectively. Since the concentration of the ternary complex (abc) must be much less than (ab), it is clear from the augmentation of the velocity produced on the addition of the catalyst that the fragility or ease of decomposition of this ternary complex must be much greater than that of the binary complex (ab), and the energy of activation correspondingly less. We have noted that in cases of bimolecular gas reactions, where activation is caused by collision, the reaction proceeds relatively rapidly when the energies of activation are not too large, as exemplified in the following data obtained by Hinshelwood.[2]

Bimolecular Reaction. Decomposition of	E cals. per grm.-mol.	$T\,ab$.	$\frac{E}{T\,ab}$.
$2N_2O$ . . .	58,500	956	61
$2HI$	44,000	760	58
$2Cl_2O$ . . .	21,000	384	55

In the above table $T\,ab$ is the temperature at which k, the bimolecular velocity coefficient, has the same value for each reaction, viz. $k = 0{\cdot}0914$ grm.-mol. per litre per second. We may thus anticipate

[1] Lowry, *J. Chem. Soc.*, 1899, **75**, 211; 1908, **93**, 119. [2] *J. Chem. Soc.*, 1925, **125**, 1843.

reactions to take place in solution at ordinary temperatures with measurable speeds when the energies of activation are small; the temperature coefficients of the catalysed reactions indicate that the energies of activation of the ternary complexes are of the order anticipated from analogy with the homogeneous kinetically activated gas reactions. The bimolecular reaction $a+b \longrightarrow c$, on the other hand, evidently requires a much larger energy of activation, and will thus proceed at ordinary temperatures at rates comparable to, say, the decomposition of nitrous oxide or the union of hydrogen and oxygen at low temperatures. We may conclude that binary complexes may be formed, but reaction does not necessarily result; thus, in the interaction between ethylene and hydrobromic acid, the complex, as shown (C_2H_4 . HBr) by Maas, is present at low temperatures in relatively large quantities, but ethyl bromide is not formed, presumably owing to the large value of the critical energy increment.

The stability of intermediate compounds.—In the foregoing discussion it has been shown that the mechanism of reaction in solutions can be most readily interpreted on the concept of unstable intermediate complexes. Thus, in the reaction $a+b \longrightarrow d$ catalysed by the catalyst c the formation of complexes by a series of reactions $a+b \longrightarrow (ab)$, $ab+c \longrightarrow (abc)$ is postulated. Whilst reaction may take place without the catalyst by the reaction

$$a+b \longrightarrow (ab) \longrightarrow d,$$

it would appear that the energies of activation are so large that such reactions do not occur in liquids at ordinary temperatures and the usual mechanism is $a+b \longrightarrow (ab)$; $(ab)+c \longrightarrow (abc) \longrightarrow d+c$, the complex (abc) being very unstable and consequently present in solutions in sub-analytical quantities.

Whilst the presence of binary complexes in strong solutions can be readily demonstrated by the various methods commonly employed for this purpose, the identification of the ternary complex which is the one actually undergoing the chemical change being measured is not such a simple matter; for, to take a specific example, we are by no means justified in the assumption that, since Kendall has demonstrated the existence of unstable compounds of the type RCOOR′ . HX, that a complex RCOOR′HX . H_2O is the actual intermediary complex in catalytic hydrolysis.

Attempts have been made to identify these unstable complexes in two ways. We may either investigate the functional relationship between the reaction velocity and the activities of all the possible reacting species so as to obtain a general expression of the type

$$\frac{dx}{dt} = K' \frac{(a)^n (b)^m (c)^o}{f(a^n b^m c^o)} f_a^n f_b^m f_c^o,$$

or we may develop, from preconceived hypotheses as to the stability of molecules of different configuration, a structure that will be readily susceptible to the reaction desired.

As an example of the former method may be cited the case o hydrogen ion catalysis in a number of reactions such as the inversion of sucrose.[1] This reaction may be regarded as proceeding through the formation of a ternary complex (sugar) · (water ^{n}) · ($\dot{H}$), since the reaction proceeds at a velocity directly proportional to the activities of the two solutes of the system; uncertainty, however, still exists as to the true value of n for the solvent, which different observers evaluate at from 2 to 6. Whilst the activity of the hydrogen ion in solution may be determined by various methods,[2] or calculated from the bulk concentration of reactants with the aid of the equations developed by Noyes and Falk,[3] Lewis and Linhart,[4] Brönsted,[5] Bjerrum,[6] or Debye and Hückel,[7] we cannot from this relationship alone determine whether the hydrogen ion forming the reaction complex is hydrated or not. Since the equilibrium $\overset{+}{H} + nH_2O \rightleftarrows (\overset{+}{H} \cdot nH_2O)$ or $\dot{H} \cdot aH_2O + bH_2O \rightleftarrows (\dot{H} \cdot nH_2O)$, where $a+b=n$, may be set up in the system, evidently either form of the hydrogen ion is available to form the reactive complex. The investigations of Lapworth [8] and Dawson,[9] as well as the numerous experiments on neutral salt action (see p. 173), have made it more than probable that it is the unhydrated or the less hydrated form of hydrogen ion is the active agent.

Again, we may note that the solvation of sucrose varies but little with the temperature, or the value of (ab) will be constant over a considerable range of temperatures. The influence of temperature on the reaction velocity will thus be largely affected by the change in the concentration of the active form of the hydrogen ion with the temperature, a conclusion arrived at by Rice.[10]

Amongst other examples of this method may be cited the decomposition of acetylchloramino benzene in the presence of hydrochloric acid as a catalyst examined by Rivett[11] and Harned and Selz,[12] and of hydrogen peroxide in the presence of hydrobromic acid examined by Bray and Livingstone,[13] where the reaction velocities of the reactions are expressible in the forms

$$(1) \quad -\frac{dc}{dt} = (C)(\dot{H})(Cl')f\dot{H}fCl';$$

$$(2) \quad -\frac{dc}{dt} = (C)(\dot{H})(Br')f\dot{H}fBr'.$$

[1] Harned, *J. Amer. Chem. Soc.*, 1915, **37**, 2467; *ibid.*, 1918, **40**, 1461; Fales and Morell, *ibid.*, 1921, **44**, 2072; McC. Lewis and Corran, *ibid.*, 1921, **44**, 1673; Scatchard, *ibid.*, 1923, **45**, 1580; McC. Lewis and Jones, *J. Chem. Soc.*, 1920, **117**, 424.

[2] Lewis and Randall, *Thermodynamics.*

[3] *J. Amer. Chem. Soc.*, 1910, **32**, 1011.

[4] *J. Amer. Chem. Soc.*, 1919, **41**, 1955.

[5] *J. Amer. Chem. Soc.*, 1922, **44**, 938.

[6] *Zeitsch. f. Elektrochem.*, 1918, **24**, 321.

[7] *Physikal. Zeitsch.*, 1923, **24**, 185, 305.

[8] *J. Chem. Soc.*, 1908, **73**, 2157.

[9] *J. Chem. Soc.*, 1911, 991.

[10] *J. Amer. Chem. Soc.*, 1923, **45**, 2808.

[11] *Zeitsch. physikal. Chem.*, 1913, **82**, 201.

[12] *J. Amer. Chem. Soc.*, 1922, **44**, 1484.

[13] *J. Amer. Chem. Soc.*, 1923, **44**, 1251, 2048.

More speculative in character is the second method of approaching this question from the supposed electrical structure of organic compounds. The problem may be exemplified in the case of the combination of ethylene and chlorine or bromine. At low temperatures these gases do not react by bimolecular collision.[1] Undoubtedly compounds are formed on collision of the type (C_2H_4 . Br_2), but the energy of activation is so high that combination to the dibromide does not occur. At high temperatures it is probable that true bimolecular reaction might result.

This reaction is, however, readily catalysed by surfaces,[2] and it is found that " polar " surfaces are more effective than non-polar surfaces ; thus, paraffin wax is, as shown by more recent unpublished experiments, quite inert as a catalyst, a water or ammonia film is more effective than cetyl alcohol, which, in turn, is somewhat less effective than stearic acid. Although it cannot be definitely stated on account of our lack of knowledge of the structure of the surfaces that " polar " groups possess different activities, it is clear that the " polar " groups are more effective than non-polar groups. This conception is an exemplification of the idea originally put forward by Armstrong[3] that chemical action is reversed electrolysis. Whilst it is clear that the catalyst has lowered the critical energy increment necessary for the union of the gases, the hypothesis of Armstrong would lead us to anticipate that the structure of the ternary complex, gases-surface, at the moment of formation must be similar in electrical properties to a cell.

Our ideas of the electrical structure of complex organic molecules are at the present time undergoing rapid changes, and on such subjects as the transmission of " polarity ", the dissociation constants of organic acids, and the structure of double bonds, opinion is sharply divided.[4] The following considerations may be put forward as a somewhat general expression of method by which it is hoped that an adequate understanding both of the nature and stability of these catalytic complexes may be ultimately arrived at. The conception of the catalyst in these liquid reactions as a charged ion leads us to consider that it is not alone the kinetic impact of collision that effects disruption, but that, in addition to the energy supplied by kinetic agitation, which solvent molecules could supply equally well, an electric distortion of the molecule is produced simultaneously. Indeed, it would appear that this electrical distortion produced, or the electrical work done in approach, is a much more important factor than the kinetic factor. There are few catalytic homogeneous gas reactions, owing to

[1] Stewart and Edlund, *J. Amer. Chem. Soc.*, 1923, **45**, 1014.

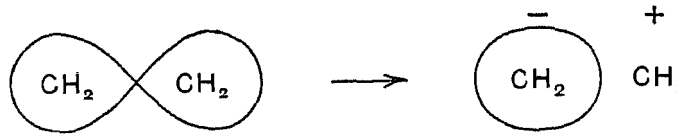
[2] Stewart and Edlund, *J. Amer. Chem. Soc.*, 1923, **45**, 1014 ; Norrish, *J. Chem. Soc.*, 1923, **123**, 3006.

[3] *J. Chem. Soc.*, 1885, p. 39 ; *ibid.*, 1893, p. 145.

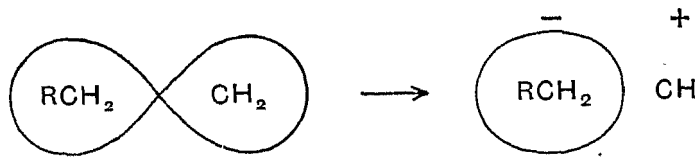
[4] See *Trans. Farad. Soc.*, 1923, for a résumé of the subject.

the absence of electric effects. The catalyst must thus form a transitory highly reactive chemical compound with the solvated reactant.

Saturation of a double bond.—Since the double bond in the ethylene molecule is broken when the dibromide is formed it is assumed by many, especially by Lowry, that activation consists in the breaking of a double bond to form a polar molecule $\overset{+}{C}H_2 - \overset{-}{C}H_2$. On the assumption that the valency electron of the bond forms a binuclear orbit this process may be represented diagrammatically as follows :

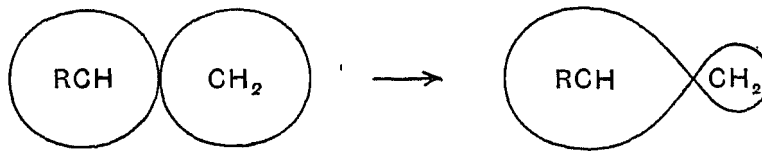


In the case of substituted unsymmetrical ethylene molecules we may represent the rupture on this point of view :



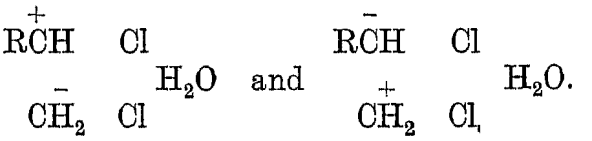
where R, the substituent group, renders the group RCH more electronegative than CH_2.

It is found, however, on the addition of substances such as HBr, that two compounds are always formed, $RCH_2 . CH_2Br$ and $RCH\,Br . CH_2$, and for this reason it has been suggested that the excited or activated ethylene molecule is not necessarily " ionised ", but that the electron travels round the two nuclei in such a way that it remains for a longer time in the orbit of the RCH than of the CH_2 group, a view which can be diagrammatically presented as follows :



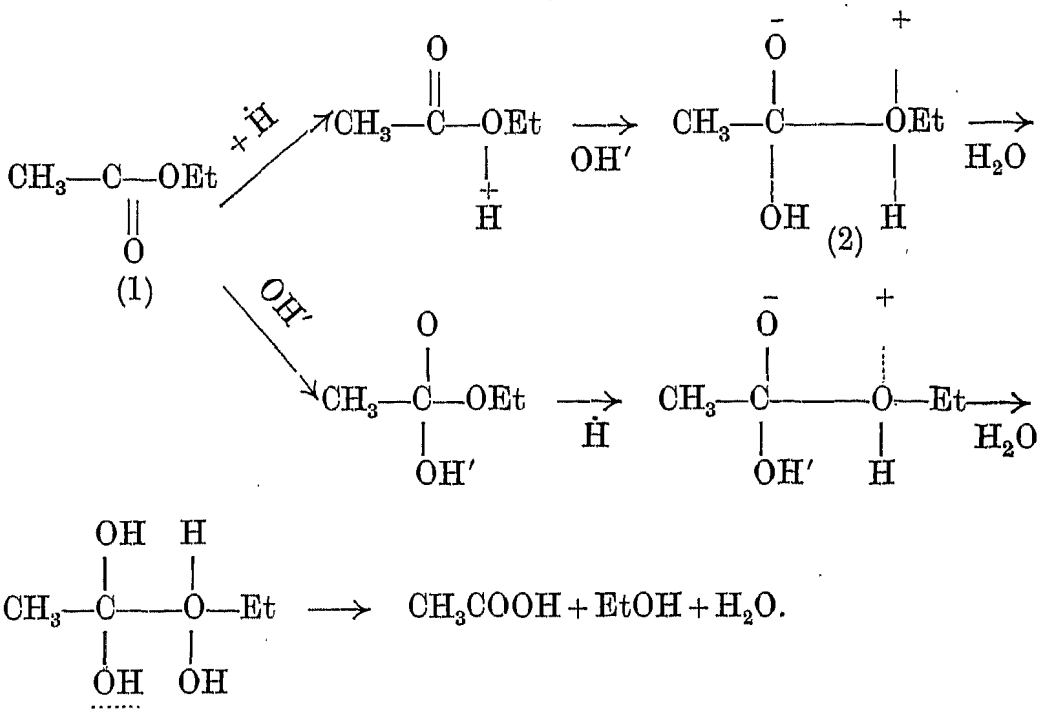
Thus the compound will be oscillating in " polarity " as the electron moves in its orbit round one focus to the other, but the $\overset{-}{R}CH$ will exist for a longer time than the $\overset{-}{C}H_2$, and the chance of reaction by collision in this form thus more favourable. As in the hydrogen chlorine combination, the halogen molecule is more easily excited in the presence of a polar molecule such as water. Reaction thus ensues between the ethylene and the halogen through the agency of water, primarily by stabilising the active form of the halogen which reacts with the ethylene when in one of its polar forms.

The activated complexes on this view would be represented diagrammatically as



Contrary to the original suggestion of ionising the double bond linkage, the catalyst merely assists in activating the halogen or halide, and by forming a complex with it which possesses a smaller energy of activation. This view could be put to experimental proof, for catalysts should not alter the ratio of the two products formed on the addition of halide acids to asymmetric substituted ethylene derivatives.

The hydrolysis of esters.—Lowry[1] has developed, on the conception of ionisation of the double bond referred to above, a mechanism to interpret the hydrolysis of esters by hydrogen or hydroxyl ions. According to this view the action of these catalysts on the ester can be diagrammatically represented as follows :

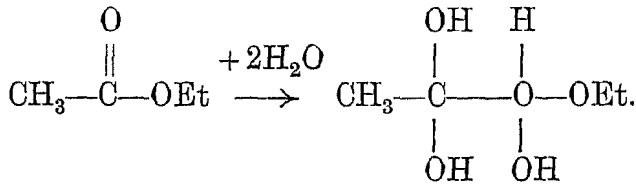


The function of the catalyst is to convert the closed form (1) of the ester into the amphoteric bipolar molecule (2) by (*a*) direct addition first of the catalytic ion, (*b*) attraction of the ion of opposite sign, thus effecting the addition of the elements of water.

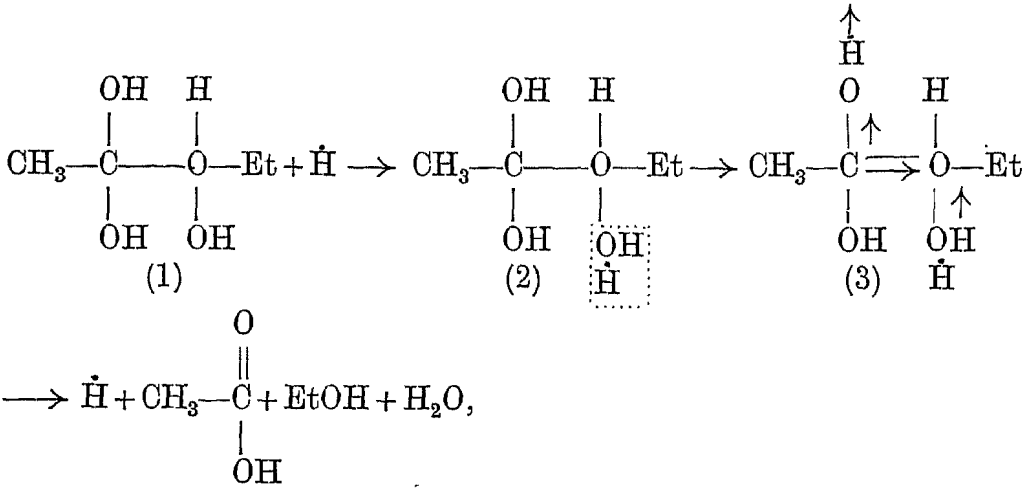
A slight modification of this view would be more in harmony with the ideas already referred to. We may regard equally well the process

[1] Solvay Conference, 1925.

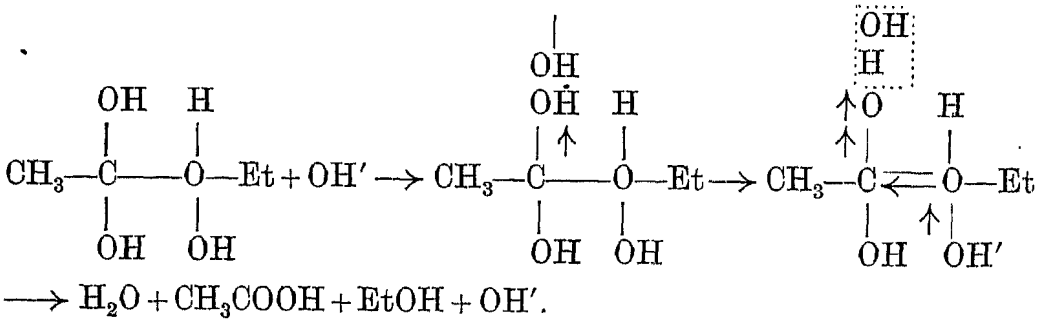
of solution of an ester in water in the absence of a catalyst as effecting the formation of a complex ester-water, according to the scheme



The unhydrated or less hydrated form of the catalytic hydrogen or hydroxyl ion can, by impact, form an unstable complex which breaks down to acid and water and hydrogen ion again as follows :



where the arrows in (3) indicate the passage of the electron effected by the collision of the stable molecule (1) with the highly active charged ion. In a similar manner we may write :



The catalytic activity of the two ions is, on this view, to be ascribed to the stable water-ester complex (1) being chemically reactive, the catalytic ion being attached at one point of the molecule and one being subsequently liberated at another point. There is definite evidence for the rapid hydration of esters and sugars in aqueous solution, the magnitude of which is, however, no criterion of subsequent speed of hydrolysis or inversion, and it is to this complex that the catalytic ion is added, another ion leaving the molecule at another

point at the moment of decomposition. That esters may be regarded as amphoteric electrolytes capable of uniting with both hydrogen and hydroxyl ions was a view originally put forward by Euler (see Chapter XIII.), who has been able to measure both the acid and basic dissociation constants in a number of cases. Whilst Euler's investigations afford a clear argument why the formation of the complex ions from the ester with either of the catalytic ions of water occurs, the reason why these are particularly reactive can only be arrived at from speculations and considerations of the nature already discussed. Many other examples of attempts to formulate the mechanism of the reaction and to account for the instability of the complexes have been investigated in this way, such as the mutarotation of the sugars and the decomposition of the chloramines.

The most detailed examination of a case of homogeneous reaction in which anions exert a catalytic action has been made by Brönsted and Pedersen,[1] who investigated the catalytic decomposition of nitramide.

Nitramide decomposes in solution according to the reaction

$$H_2N_2O_2 \longrightarrow H_2O + N_2O;$$

the decomposition is strongly catalysed by anions which may here be represented as hydrogen ion acceptors and the mechanism of reaction depicted as follows:

$$H_2N_2O_2 + A' \longrightarrow (A'\overset{+}{H}) + HN_2O_2' \longrightarrow OH' + N_2O.$$

In aqueous and in slightly acid solution nitramide undergoes a slight decomposition which is unaffected by the nature or strength of the acid present; this spontaneous decomposition may be regarded as a measure of the basicity of the water with which the nitramide reacts, according to the reaction

$$H_2N_2O_2 + H_2O \longrightarrow \overset{+}{H}_3O + HNO_2' \longrightarrow \overset{+}{H}_3O + OH' + N_2O.$$

If the concentration of the nitramide be x the reaction velocity in aqueous solution will be

$$-\frac{dx}{dt} = kx.$$

In the presence of a catalyst of concentration c we obtain

$$-\frac{dx}{dt} = kx + k'cx,$$

or by

$$\frac{x}{x_0} = \{k + k'c\}t.$$

In aqueous solution it is found to be ·000385 at 15° C. with a half life of 13·2 hours.

[1] *Zeitsch. physikal. Chem.*, 1924, **108**, 185.

Brönsted and Pedersen have examined the catalytic activity of t anions of a number of organic acids by determining the rate of reacti in the presence of their salts, together with sufficient acid to preve the formation of hydroxyl ions by hydrolysis of the salt. In t following table are given the catalytic activity of the anions investigate together with the dissociation constants of the acids. It is interesti to note an empirical relationship between these two properties.

Acid.	Dissociation Constant K.	Velocity Constant k'.	$k'K^{0.83}$.
Propionic	$1{\cdot}34\ 10^{-5}$	0·65	$5{\cdot}9\ 10^{-5}$
Acetic	$1{\cdot}8\ 10^{-5}$	0·50	5·8
Phenylacetic . . .	$5{\cdot}3\ 10^{-5}$	0·23	6·5
Benzoic	$6{\cdot}5\ 10^{-5}$	0·19	6·3
Formic	$2{\cdot}1\ 10^{-4}$	0·082	7·2
Salicylic	$1{\cdot}0\ 10^{-3}$	0·021	6·2
Dichloracetic . . .	$5{\cdot}0\ 10^{-2}$	0·0007	5·8
		Mean	$6{\cdot}2\ 10^{-5}$

They have also extended their investigations to the anions of t polybasic acids. Thus, in the case of salts of dibasic acids there a present in solution two anions governed by the equilibria

$$H_2X \rightleftarrows \dot{H} + HX' \quad k_1,$$
$$HX' \rightleftarrows X'' + \dot{H} \quad k_2;$$

the velocity of decomposition is accordingly given by the expression

$$\log \frac{x}{x_0} = \{k + k_1c_1 + k_2c_2\}t,$$

where k' and k'' are the catalytic constants of the anions HX' and X respectively.

The results obtained were exceedingly interesting in the light the probability of dissociation in the two stages.

If we compare the dissociation of the two acids, caprylic and suberi

$$C_7H_{15}COOH \longrightarrow C_7H_{15}COO' + \dot{H} \qquad K = 1{\cdot}44\,.\,10^{-5}$$

$$C_6H_{12}\begin{matrix}COOH\\COOH\end{matrix} \longrightarrow C_6H_{12}\begin{matrix}COO'\\COOH + \dot{H}\end{matrix} \qquad K_1 = 3{\cdot}0\,.\,10^{-5},$$

we may regard the resultant dissociation constants which stan in the ratio of 1 : 2 from a purely statistical point of view. W can assume that the organic ions of each acid are equally hydrophil in character, the probability of each acid losing a hydrogen ion fro one carboxyl group and its recombination being equal. The dibas acid, however, can lose a hydrogen ion from either carboxyl grou

ut combination can only occur with the group which has lost the ion; consequence, we might anticipate that the dissociation constant hich represents the ratio of the speeds of dissociation and recombination would be twice as great for the dibasic acid as for the monobasic cid, a conclusion justified by the experimental data. If we now ompare the monobasic acid with the dissociation of the dibasic acid its second stage,

$$C_7H_{15}COOH \rightleftarrows C_7H_{15}COO' + \dot{H}$$

$$C_6H_{12}\begin{matrix}COO'\\COOH\end{matrix} \rightleftarrows C_6H_{12}\begin{matrix}COO'\\COO'\end{matrix} + \dot{H},$$

nd again assume the two ions to be equally hydrophilic in character, is clear that the probability of dissociation for each acid is identical, ut the chance of recombination is twice as great for the dibasic acid for the monobasic acid. We thus obtain what may be termed a atistical factor regulating the degree of dissociation of polybasic ids in which the anions are equally hydrophilic. These factors are own in the following table:

Dissociation.	Statistical Factor n.
$HQ \rightleftarrows \dot{H} + Q'$ . .	1
$H_2Q \rightleftarrows HQ' + \dot{H}$ . .	$\frac{1}{2}$
$HQ' \rightleftarrows Q'' + \dot{H}$ . .	2
$PH_3 \rightleftarrows PH'_2 + \dot{H}$ . .	$\frac{1}{3}$
$PH'_2 \rightleftarrows PH'' + \dot{H}$ . .	1
$PH'' \rightleftarrows P''' + \dot{H}$ . .	3

In the light of these considerations the data of Brönsted and Pedersen r dibasic acids and the tribasic phosphoric acid show a remarkable niformity, as is clear from the following table:

Acid.	K_1.	n.	k'.	$k'(nK_1)^{0\cdot 33}$.	K_2.	n.	k''.	$k''(nK_2)^{0\cdot 33}$.
Phosphoric	$8\cdot9\ 10^{-3}$	$\frac{1}{3}$	0·0079	$6\cdot3\ 10^{-5}$	$4\cdot9\ 10^{-8}$	1	86	$7\cdot2\ 10^{-5}$
Tartaric .	$9\cdot7\ 10^{-4}$	$\frac{1}{2}$	0·0363	$6\cdot3\ 10^{-5}$	$3\cdot7\ 10^{-5}$	2	0·165	$6\cdot2\ 10^{-5}$
Succinic .	$6\cdot5\ 10^{-5}$	$\frac{1}{2}$	0·320	$6\cdot0\ 10^{-5}$	$2\cdot1\ 10^{-6}$	1	1·86	$6\cdot2\ 10^{-5}$
Malic .	$4\cdot0\ 10^{-4}$	$\frac{1}{2}$	0·0765	$6\cdot4\ 10^{-5}$	$6\cdot9\ 10^{-6}$	2	0·72	$6\cdot8\ 10^{-5}$
			Mean value	$6\cdot2\ 10^{-5}$			Mean value	$6\cdot4\ 10^{-5}$

It is clear that the catalytic decomposition of nitramide in the esence of the salts of various polybasic acids permits us to obtain formation on the statistical factors of these acids as well as their ssociation constants. For the dissociation of non-symmetrical basic acids, the effect of asymmetry on the statistical factor might

be determined from experimental values of k'', the catalytic constant of the dibasic anion, and the value $6{\cdot}2\ 10^{-5}$ of the constant $k''(nK_2)^{0{\cdot}83}$.

The method permits of several interesting applications. Thus, they have investigated a typical pseudo-acid in the form of nitrourethane which, as shown by Hantzsch,[1] can exist in two forms:

$$\underset{\text{Isonitrourethane.}}{NO_2-NH-COOC_2H_5} \rightleftarrows \underset{\text{Nitrourethane.}}{C_2H_5OOC-N=N.OOH.}$$

The acid form can undergo dissociation yielding a catalytic anion $C_2H_5OOC-N=NOO'$, which was found to yield a catalytic constant of 0·0066. From conductivity data the dissociation constant K is found to be $4{\cdot}3\ .\ 10^{-4}$,[(2)] whence the constant $kK^{0{\cdot}83}$ is found to be $1{\cdot}08\ 10^{-5}$, or some six times smaller than the value obtained for the other acids. It must be concluded that the true strength of the acid nitrourethane is some eight times greater than the value observed with the pseudo-acid in solution.

Again, since the decomposition rate of nitramide is dependent on the presence of hydrion acceptors in the solution, all substances which function as bases in this sense are catalytically active. We have already noted that water may be regarded as a base in that it can accept hydrogen ions and does in fact possess a small catalytic activity.

The catalytic activity constant of aniline was found to be $k=0{\cdot}531$. Brönsted and Pedersen point out that the value of the dissociation constant of the ion

$$C_6H_5NH_2\dot{H} \rightleftarrows C_6H_5NH_2+\dot{H} \quad K=2{\cdot}0\ .\ 10^{-5}$$

is very close to that of acetic acid,

$$CH_3COOH \rightleftarrows CH_3COO'+\dot{H} \quad K=1{\cdot}8\ .\ 10^{-5},$$

and, as will be noted, the specific catalytic activities are almost identical. The values for many hydrogen ion acceptors are shown in the following table:

	K.	k.
Water	?	0·00038
Aniline	$2{\cdot}0\ 10^{-5}$	0·531
Quinoline	$1{\cdot}2\ 10^{-5}$	1·9
Dimethylaniline . .	$6{\cdot}3\ 10^{-6}$	2·7
Pyridine	$4{\cdot}4\ 10^{-6}$	4·6

The effect of neutral salts in increasing the ionic activity is well exemplified in the case of the addition of potassium nitrate to propionic acid, in which the following data were obtained:

C_{PH}	0·101	0·101	0·101	0·101
C_{KNO_3}	0	0·02	0·05	0·1
$k\ 10^5$	114	125	128	132
$\{k-k_{H_2O}\}\ 10^5$ . .	76	87	90	94
$C_P\ 10^3$	1·17	1·34	1·38	1·44
$K\ 10^5$	1·37	1·80	1·90	2·07

[1] *Ber.*, 1899, **32**, 575, 3066.

[2] Bauer, *Zeitsch. physikal. Chem.*, 1897, **23**, 409.

CHAPTER IV

THE THEORY OF HETEROGENEOUS CATALYTIC REACTIONS

ETEROGENEOUS catalytic reactions are those that take place at rfaces. Whilst many examples of reactions are known which occur ther at solid-gas or solid-liquid interfaces, but few cases of catalytic actions at liquid-gas interfaces have been established with certainty, though Rideal and Wolf [1] have examined the destruction of rennin an air-liquid interface, and Norrish and Rideal [2] the catalytic influence oxygen at a liquid sulphur-hydrogen interface. There is, however, tle reason to doubt that the specific effects due to the properties herent at all interfaces will have their influence on reactions taking ace at liquid surfaces.

Of fundamental importance in the theory of the mechanism of terogeneous catalytic actions is the existence of an interfacial surface ergy. In the case of liquid-gas or liquid-liquid interfaces the free surce energy σ is readily determined by various experimental methods, d from a knowledge of this value as well as the temperature coefficient the surface energy $\frac{d\sigma}{dT}$ the total surface energy u may be calculated th the aid of the Gibbs-Helmholtz equation

$$\sigma - u = T\frac{d\sigma}{dT}.$$

e must postulate the existence at the interface solid-gas or solidquid of a similar surface energy, although, owing to the immobility one phase, its value cannot readily be determined. The existence such a surface energy in solids is in fact confirmed by the phenomenon cohesion, for, on cutting a crystal, two surfaces are formed in which e previously locked cohesive forces are now unsaturated. In general, e surface atoms of a solid are situated unsymmetrically to the forces cohesion as compared with the internal ones. Attempts have been ade to compute the surface energy of solids by indirect methods. n the supposed analogy between small crystals and small drops, the

[1] *Proc. Roy. Soc.*, 1924, **97A**, 106.
[2] *J. Chem. Soc.*, 1923, **123**, 696; 1924, **125**, 1689, 3203, 2070.

increase in solubility of a crystal as a reciprocal function of its radius has been utilised for this purpose. Although the analogy may be criticised, the magnitudes of the values obtained are by no means unreasonable.

Since, in systems not in equilibrium, reactions may proceed associated with a decrease in free energy, if adsorption (at an interface) of constituents present in a fluid bulk phase is associated with a decrease in the free surface energy, such a reaction will ensue. We shall have occasion to note that this property of adsorption is common to all interfaces, that at liquid interfaces the magnitude of the effect depends only on the properties of the system, but at solid surfaces the physical structure as well as the chemical properties of the surface have to be taken into consideration.

Adsorption at liquid interfaces.—On the addition of a solute to a liquid a change in the surface energy of the liquid occurs. If the added solute has the effect of diminishing the surface energy, the concentration of the solute in the surface film will be greater than that in the bulk of the liquid. The quantitative relationship between the excess concentration of the surface film over the bulk of the solution and the lowering of the surface tension has been developed by W. Gibbs and Sir J. J. Thomson. In its simplest form we may express this relationship as follows :

$$\Gamma = -\frac{d\sigma}{df},$$

where Γ is the excess surface concentration in grm.-mols. per sq. cm.,
σ the surface tension,
f the chemical potential of the solute.

If the solute obeys the laws of ideal solution, then

$$f = f_0 + RT \log c,^1$$

whence

$$\Gamma = -\frac{1}{RT}\frac{d\sigma}{d \log c} = -\frac{c}{RT}\frac{d\sigma}{dc}.$$

Similarly for those cases in which the solute elevates the surface tension of the liquid there will be a smaller concentration of solute in the surface film than in the bulk of the liquid.

We are thus in a position to calculate the composition of the surface film, frequently termed the Gibbs layer. We have not, however, made any assumptions as to the thickness of the film in which the forces of surface tension produce a modification in chemical composition. We shall have occasion to observe that the investigations of Lord Rayleigh, Langmuir, Devaux, Labrouste, and N. K. Adam on the effect of insoluble fatty acids and their derivatives on the surface tension of water, make it practically certain that these substances

[1] For non-ideal solutions $f = f_0 + RT \log a$ or $= f_0 + RT \log \gamma c$, where γ is the actively coefficient and a the thermodynamic activity.

spread over a water surface in a unimolecular layer. For soluble substances, direct evidence for the unimolecular character of the Gibbs layer is not forthcoming, but it may be concluded that in many cases such an assumption is justified. The evidence for this assumption is twofold. In the first case, as pointed out by Langmuir, if it be assumed that the Gibbs layer is unimolecular in character the limiting areas per molecule for organic substances, which are adsorbed at the interface, calculated with the aid of the Gibbs equation, are in good agreement with the areas anticipated from other considerations. Again, if molecules of the solute are positively adsorbed at the interface we may regard the lowering of the surface tension of the pure solvent by the solute $F = \sigma_0 - \sigma_{\text{solution}}$ as being due to the kinetic agitation of the adsorbed solute molecules on the surface; thus F will be analogous to a two-dimensional osmotic or gas pressure. This suggestion, originally put forward by Traube, was rejected by later investigators, notably by Milner and V. Sczyskowski, for the law $FA = RT$, the two-dimensional equivalent to the three-dimensional law $PV = RT$, was found not to express the observed relationship between F and A, where F is defined as above and A as $\frac{1}{\Gamma}$.

A more careful examination of the state of this two-dimensional solution, however, by Schofield and Rideal[1] has indicated that the surface solutions are always relatively concentrated and may be regarded as equivalent to gases at high pressures or to strong solutions. The two-dimensional analogue of Amagat's equation of state,

$$F(A - B) = xRT,$$

where B is the limiting area and $\frac{1}{x}$ the coefficient of association, is found to agree with the experimental data, and the FA curves of solutions of fatty acids and esters are found to reproduce to a surprising degree of accuracy the PV curves for gases such as nitrogen and ethylene.

Whilst on surfaces of most liquids the Gibbs layer is but unimolecular in thickness, it cannot be said that the adsorbed solute possesses all the properties of the pure solute in bulk. Thus, saturation of the Gibbs layer in the case of ethyl alcohol-water mixtures occurs at a concentration of 0·3 molar, yet the surface phase, although consisting of pure ethyl alcohol, is by no means identical in properties with a free surface of ethyl alcohol. Even more definite in this direction are the experiments of Iredale[2] on the adsorption of vapours on the surface of mercury. Whilst the surface tension of mercury is lowered very markedly by the adsorption of a unimolecular layer of vapour such as ethyl acetate, benzene, or water, and the lowering is more pronounced

[1] *Proc. Roy. Soc.*, 1925, **107A**, 57.
[2] *Phil. Mag.*, 1923, **45**, 1099; **48**, 165, 1727.

the more closely packed the unimolecular film on the surface, yet the vapour pressure of even a closely packed unimolecular film is less than that over the pure liquefied vapour at the same temperature.

From these and Iredale's experiments we may conclude that the building up of the primary Gibbs layer is associated with a marked change in the surface energy of the liquid adsorbent, and that the building up of the secondary films or diffuse layer is associated with a further definite but very much smaller decrease in free energy.

In dealing with the adsorption of vapours and liquids by solids, we shall again have occasion to note that the formation of what may be termed the primary film, unimolecular in character, is associated with large thermal effects, but that in many cases secondary film formation, which may be multimolecular in thickness, also takes place.

Evidence for molecular orientation in adsorption at liquid surfaces.—The work commenced by the late Lord Rayleigh [1] and developed by Hardy,[2] Marcelin,[3] Langmuir,[4] Labrouste,[5] Harkins,[6] N. K. Adam,[7] and others, on the surface tension of solutions has given us a deeper insight into the mechanism of adsorption, the bearing of which on catalytic processes is of fundamental importance.

If we bring two liquid surfaces together of surface tensions σ_A, σ_B to form an interface of surface tension σ_{AB} there will be a certain decrease in the free energy of the system given by the expression

$$W = \sigma_A + \sigma_B - \sigma_{AB}.$$

In the following table are summarised some of the values for this decrease in free energy when various liquids are brought into contact with water and mercury.

Substance.	W. with Water.	W with Mercury.
	Ergs. per sq. cm.	Ergs. per sq. cm.
Pentane	18·9	..
Hexane	20·6	60·8
Octane	21·6	65·5
CCl_4	24·0	74·8
Water	73	91·5
Ethyl iodide	..	110
Methyl iodide	..	110
Carbon disulphide	21	90
Ethyl ether	39·9	..
Alcohols	47·8-51·8	..
Organic acids	46-50	..
Ethyl esters	37-46	..

[1] *Proc. Roy. Soc.*, 1890, **47**, 281; *Phil. Mag.*, 1899, **48**, 331.
[2] *Proc. Nat. Acad. Sci.*, 1917, **3**, 141; *Proc. Roy. Soc.*, 1912, **86**, 610; 1913, **8**, 313.
[3] *J. de Physique*, 1914, **1**, 19.
[4] *J. Amer. Chem. Soc.*, 1917, **39**, 1868.
[5] *Ann. d. Phys.*, 1920, **14**, 164.
[6] *J. Amer. Chem. Soc.*, 1917, **39**, 354.
[7] *Proc. Roy. Soc.*, 1921, **99A**, 336; 1922, **101**, 452; 1922, **101**, 517; 1923, **103**, 677.

It is evident that the decrease in free energy when a liquid is brought into contact with water or mercury is most marked when the former contains certain reactive groupings such as the halide, sulphide, and hydroxyl for mercury, and the hydroxyl, oxonium, and carboxyl for water.

The decrease in free energy is the result of the action of the adsorption forces between the surface layers of the two liquids, and it is evident that these adsorptive forces operate on a specially reactive part of the molecule. Thus in the case of fatty acids floating upon the surface of water we should anticipate that the acid would be anchored to the water by means of the carboxyl group, since the hydrocarbon chain possesses but little adhesion for water.

Direct confirmation of this hypothesis has been obtained by measurement of the surface tension of water to which definite amounts of the highly insoluble long-chain fatty acids, alcohols, and substituted ureas dissolved in benzene have been added. If a definite quantity of fatty acid, *e.g.* palmitic acid, be dissolved in benzene and dropped upon the surface of water, after the evaporation of the benzene the water will be covered with a layer of palmitic acid and the surface tension of the water will be lowered. If the lowering of the surface tension be plotted against the area of the water covered with this amount of palmitic acid, a curve of the following form will be obtained.

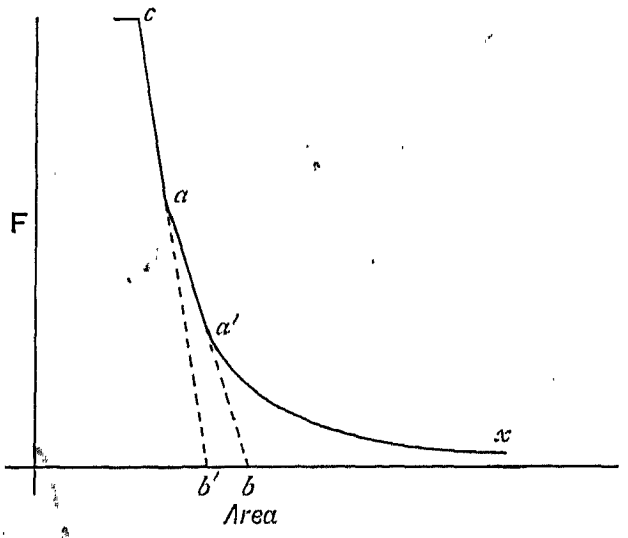


FIG. 2.

It will be noted that the curve is divisible into three parts, a linear portion *ca*, a second linear portion *aa'*, and a curved portion *a'x*. The explanation of the curve obtained is readily understood from the following arguments.

If a small quantity of fatty acid be allowed to expand over a wide area of water the *F*, *A* relationship will be defined by some point on the curve in the region *a'x*. On contracting the area the force, *i.e.*

the apparent lowering of the surface tension, increases but slowly until, at the point a', it rises rapidly in a linear manner. At the point a, under higher compressions, there is a break in the curve, which proceeds again in a linear manner to the point c, where an abrupt change in the surface tension is noted.

From a knowledge of the number of molecules of fatty acid placed on the measured area of water, the mean area per molecule on the assumption of a unimolecular film corresponding to the pressures a' and a can readily be determined. The prolongation of the ca curve to b' gives us as the area per molecule ob' 21 Å. of ob 25·2 Å. The interesting points in connection with these measurements are, firstly, that, on the assumption that the density of palmitic acid in the thin film is identical with that in the bulk, the covering power of the fatty acid, from our knowledge of the approximate sizes of the molecules, confirms our previous hypothesis of a unimolecular layer of fatty acid molecules on the surface of the water. The second point of interest is that if similar curves for other long-chain fatty acids be made, the areas per molecule corresponding to the pressures at a and a', *i.e.* at the breaks in the curve, are identical with those of palmitic acid, as is exemplified in the following data of N. K. Adam:

Acid.	ob' in Å.	ob in Å.
Myristic	21·0	25·1
Pentadecylic	21·0	25·1
Stearic	21·0	25·1
Behenic	21·0	25·1

All these carbon chain acids have a different number of carbon atoms in their chain, yet, under corresponding compressions in a surface film, occupy identical areas. We can thus conclude (Langmuir) that all the molecules of each acid, under these compressions at any rate, are orientated in a vertical plane to the water surface and thus present equal cross-sectional areas to the lateral compressional force.

On this assumption of a vertical orientation of the molecules we must account for the fact that the molecule of the fatty acid apparently possesses two parts of different area under zero compression $ob' = 21$ Å., $ob = 25$ Å. possessing different compressibilities. These, as N. K. Adam has pointed out, correspond to the hydrocarbon chain ob' and the carboxyl head ob'. The area ob' of 21 Å. should thus be a measure of the cross-section of a hydrocarbon chain. Now the molecular volume $V_{CH_2} = 17{\cdot}8$ c.c. at the m.p. and the distance between the carbon atoms in a diamond is 1·52 Å., hence the area of a CH_2 group is *ca.* $\frac{17{\cdot}8}{N.\ 1{\cdot}52\ 10^{-8}} = 19{\cdot}3$ Å., in fair agreement with the observed value.

If the area 25·2 Å. corresponds to that of the carboxyl head immersed in the water, the replacement of this head to the molecule by other groups should give different values to ob. Some of N. K. Adam's values for the areas of various heads are given below:

Head Group.	Area in Å.U.
—COOH	25·1
—C=CH . COOH	28·7
—NH—CO—NH_2	26·3
—$CONH_2$	<21·5
—$COOC_2H_5$	22·3
—CH_2OH	21·7
—CH_2CN	27·5
—C$_6$H$_4$OH	23·8
—C$_6$H$_4$$NH_2$	23·7
—C$_6$H$_4$—$NHCOCH_3$	28·2 below 24° 25·8 above 29°
—C$_6$H$_4$—OCH_3	23·8

These conclusions, based on the study of films of relatively insoluble organic compounds on the surface of water, which have been amply confirmed and extended in various directions, go far to substantiate

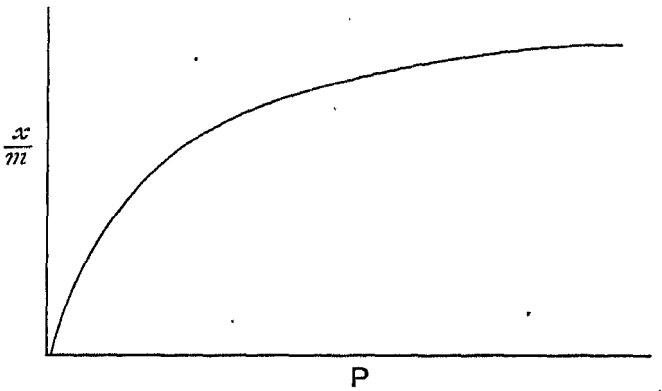


FIG. 3.

the statement that the molecules in the Gibbs film are definitely orientated and attached to the adsorbing agent by a specific (or more than one) point of attachment.[1]

Adsorption at solid interfaces.—The adsorption or surface saturation of a solid by a gas or vapour is frequently complicated by processes of solution to form either a solid solution or an actual chemical compound with the adsorbate. Again, in the case of many porous materials, the pores or capillaries of the solid, when of small diameter, offer a by no means negligible resistance to the flow of gas, in consequence of which penetration may proceed for prolonged periods of time.

As has already been indicated, owing to the existence of a surface energy in solids, we should anticipate, on analogy with liquid interfaces, the adsorption of gases or vapours if attended with a diminution of

[1] It may be noted that the polar head of a film on a water surface is not necessarily attached to only one water molecule. From a study of gel formation it appears more than probable that a cluster of water molecules are attached to the "hydrated" polar head.

the free surface energy of the surface. In addition, substances possessing a high specific surface and a concomitant surface energy, such as charcoal, will be valuable adsorbing agents.

The general asymptotic form of curve connecting gas or vapour pressure p with the amount adsorbed x, per m grms. of adsorbate, is shown on p. 65.

Many attempts have been made to express these curves in mathematical form and to interpret the mechanism of such adsorption, accurate data on the adsorption of gases by charcoal being available.[1] As a good approximation the equation of Freundlich may be applied to the experimental data.

Freundlich's isotherm equation may be expressed in the form

$$\frac{x}{m} = ap^{\frac{1}{n}},$$

or

$$\log \frac{x}{m} = a + \frac{1}{n} \log p,$$

where x is the amount adsorbed by m grms. of material under a partial pressure p, a and n being constants.

The value of n varies markedly, not only with the nature of the gas but also with the composition of the adsorbent, as is exemplified by the following figures for adsorption of gases at 20° C.:

Gas.	$\frac{1}{n}$ Charcoal.	$\frac{1}{n}$ Glass.
CO_2 . . .	0·394	0·66
NH_3 . . .	0·437	0·53
SO_2	0·324	0·28
$CHCl_3$ . . .	0·122	..
N_2O . . .	..	0·49

The two constants a and n also vary with the temperature, and it is significant to note that n approaches unity on elevation of the temperature or for low gas pressures. Thus, Chappuis[2] obtained a value of $\frac{1}{n} = 0{\cdot}84$ for the adsorption of ammonia by charcoal between 3 and 5 millimetres of mercury, whilst Travers[3] gives the following data for the adsorption of carbon dioxide by charcoal:

Temp. °C.	a.	$\frac{1}{n}$.
−78 . . .	14·29	0·133
0 . . .	2·96	0·333
35 . . .	1·236	0·461
61 . . .	0·721	0·477
100 . . .	0·324	0·518

The Freundlich isotherm leads us to the conclusion that a definite area of adsorbing surface may adsorb an indefinitely large amount of

[1] Vater, *Zeitsch. f. Elektrochem.*, 1912, **18**, 724; Travers, *Proc. Roy. Soc.*, 1915, **78A**, 9; Homfray, *Zeitsch. physikal. Chem.*, 1910, **71**, 139, 687; Titoff, *ibid.*, 1910, **74**, 641; Geddes, *Drude's Ann.*, 1909, **29**, 197; Richardson, *J. Amer. Chem. Soc.*, 1917, **38**, 1818.

[2] *Wied. Ann.*, 1883, **19**, 29.

[3] *Loc. cit.*

ıs, provided that the pressure is sufficiently high. This conclusion not justified by experiment, as a definite saturation value, frequently ell defined, has been found to exist in a great number of cases. rrhenius [1] and Schmidt [2] were the first to introduce the concept of definite saturation value for the case of an adsorbent exposed to a ıs, the equation developed,

$$\log_{10}\frac{S}{S-x}-0{\cdot}434\frac{x}{x}=\frac{p}{K},$$

ntaining two constants, S the saturation value and K, an equation hich is likewise valid over a fairly wide range of pressures.[3] The ılues of S for charcoal for various gases is somewhat significant.

Gas.	S. c.c. at N.T.P. per grm.	Gas.	S. c.c. at N.T.P. per grm.
NH_3 . .	158	CO_2 . . .	60
C_2H_4 . .	58	O_2 . . .	87
CO . . .	116	N_2 . . .	90
CH_4 . .	91	Ar . . .	87

Langmuir [4] also arrived at the conclusion that the Freundlich otherm does not represent the adsorption pressure relationship to ıy degree of accuracy. As has already been indicated, the surface a solid may be regarded as an adsorbing lattice-work of atoms. If finitely crystalline, the number of such adsorbing centres may be mputed from the atomic diameters, whilst if the surface be irregularly ystalline or amorphous, the number of these elementary spaces per uare centimetre cannot be determined directly.

We may regard adsorption as the result of an equilibrium arrived between two definite and distinct processes, condensation and aporation. If a gas molecule or atom strikes an empty space on e adsorbing surface it condenses and is held there for a period of ne. It is here subject to molecular collisions, and the kinetic energy translation will in time reach such a value that it is capable of eaking away from the surface again and evaporating. In consider- g a number of such condensed molecules or atoms we are evidently stified in speaking of the average life of an atom on the surface (τ), ıich may vary from a small fraction of a second in cases where the sorbing forces are small and the temperature high to almost in- finite periods where the conditions are favourable, as is exemplified the following data [5] for the adsorption of carbon monoxide on atinum.

[1] *Nobel Inst.*, 1911, **2**, 7. [2] *Zeitsch. physikal. Chem.*, 1912, **78**, 607.
[3] See also Williams, *Proc. Roy. Soc. Edinburgh*, 1919, 287.
[4] *Phys. Rev.*, 1916, **8**, 149; *Proc. Nat. Acad. Sci.*, 1917, **3**, 141; *J. Amer. Chem. Soc.*, 1918, 1360. [5] Langmuir, *Trans. Farad. Soc.*, 1922, **17**, 642.

Temp. °K.	Average Life in Seconds.
1000	0·00001
900	0·00004
800	0·00038
700	0·0066
600	0·30
500	63
450	2100
400	$1{\cdot}9 \cdot 10^5$
350	$5{\cdot}8 \cdot 10^7$
300	$1{\cdot}2 \cdot 10^{11}$

From a series of experiments it was established that the number of molecules reflected without condensation and re-evaporation was small, as exemplified in the following table,[1] in which the accommodation factor (a) or the fraction condensed and then evaporated is given :

Gas.	Surface.	(a).
H_2	Smooth Pt.	0·36
CO_2	,,	0·87
H_2	Pt. black	0·71
CO_2	,,	0·98

We may thus regard all molecules hitting the surface as condensing there. The rate at which a gas at a pressure p will condense on a square centimetre of condensing surface may be determined with the aid of the well-known effusion equation of Herz and Knudsen :

$$\mu = 43{\cdot}75\ 10^{-6}\frac{p}{\sqrt{MT}},$$

where μ is the number of grm.-molecules striking per sq. cm. per sec. ;
p the pressure in bars (10^6 bars = 1 atmosphere) ;
M the molecular weight of the gas ;
T the absolute temperature.

At equilibrium we must consider a definite fraction of the surface covered with adsorbed gas θ', and a definite fraction bare, θ, then we have

$$\theta + \theta' = 1. \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The rate of condensation on the uncovered portion θ is $\alpha\mu\theta$, where α is the coefficient of accommodation, which is in general nearly unity.

The rate of evaporation from the covered area θ' can be written $\nu\theta'$, where ν is the rate of evaporation per square centimetre. At equilibrium the rates of condensation and evaporation must be equal, or

$$\alpha\mu\theta = \nu\theta', \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

whence

$$\theta' = \frac{\alpha\mu}{\nu + \alpha\mu}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

If we put

$$\frac{\alpha}{\nu} = \sigma,$$

then

$$\theta' = \frac{\sigma\mu}{1 + \sigma\mu}.$$

[1] Knudsen, *Ann. Physik*, 1911, **34**, 593 ; Soddy and Berry, *Proc. Roy. Soc.*, 1911, **84**, 576.

If x grm.-mols. are adsorbed per unit area, the number of elementary spaces occupied will be $\frac{Nx}{N_o}$, where N is the Avrogadro number $= 6{\cdot}065\ 10^{23}$ molecules per grm.-mol. and N_o the number of elementary spaces per square centimetre. Whence

$$\frac{Nx}{N_o} = \theta' = \frac{\sigma\mu}{1+\sigma\mu},$$

whence

$$x = \frac{abp}{1+ap},$$

a and b being constants, or

$$\frac{p}{x} = \frac{1}{ab} + \frac{p}{b},$$

being Langmuir's equation for the adsorption isotherm. At low pressures $\sigma\mu$ will be small compared with unity. Hence

$$x = abp,$$

or the amount adsorbed will be proportional to the pressure. The amount adsorbed decreases rapidly with the temperature, since the rate of evaporation varies rapidly with the temperature.

At high pressures $\sigma\mu$ is large compared with unity, or

$$x = b.$$

We thus obtain a saturation value for the amount adsorbed. Saturation according to Langmuir's hypothesis is evidently obtained when the surface of the adsorbent is covered with a layer of the gas one molecule thick. Langmuir, in support of this hypothesis that saturation is obtained with a unimolecular layer, measured the adsorption of various gases on mica and platinum at low pressures. In the cases examined, with the exception of carbon monoxide on platinum surface, saturation was obtained with less than a unimolecular film, and the form of the p, x curve could be expressed with the aid of the equation given above. The best experimental evidence of saturated surfaces has been obtained in the study of adsorption of gases by catalytic agents. The adsorption of hydrogen by nickel, studied by Gauger and Taylor,[1] of hydrogen and carbon monoxide on copper by Pease,[2] and Hurst and Rideal,[3] of hydrogen and carbon monoxide on platinised asbestos as determined by Pollard,[4] all show saturation of the surface at pressures markedly less than 1 atmosphere at ordinary temperatures. Taylor[5] has shown that this ready attainment of saturation is consistent with the high heats of adsorption of these gases by the metallic catalysts. The experimental data also lead to interesting conclusions concerning the

[1] *J. Amer. Chem. Soc.*, 1923, **45**, 720.
[2] *Ibid.*, 1923, **45**, 1193, 2297.
[3] *J. Chem. Soc.*, 1924, **125**, 685, 594.
[4] *J. Phys. Chem.*, 1923, **27**, 365.
[5] 3rd Report on Cont. Cat., *J. Phys. Chem.*, 1924, **28**, 931.

surface of the catalyst, which are discussed in detail in a subsequent section.

The premises on which the various adsorption isotherm equations have been developed are different. In those of Freundlich and Arrhenius we tacitly assume that adsorption is a process akin to surface condensation, resulting in the formation of an atmosphere of condensed vapour and even liquid around the adsorbing material, the adsorbed film density decreasing presumably exponentially as we proceed from the surface until it is identical with the circumambient vapour. Langmuir assumes as a premise that the range of molecular action is limited to one molecule in thickness, and that the film is in consequence but one molecule thick.

Direct confirmation of either hypothesis in the case of charcoal is scarcely possible, owing to the uncertainty in the evaluation of the specific surface. Many measurements, however, have been made for the adsorption of vapours, *e.g.* water, benzene, chloroform, on the surfaces of glass, sand, quartz, and some metals, and in these cases the multimolecular nature of the adsorbed film has been substantiated.[1] The direct experimental evidence for the amount of gas adsorbed is thus by no means conclusively in favour of the general application of Langmuir's hypothesis.

We may, as Langmuir has suggested, attempt to avoid this difficulty by assuming that in those cases where a multimolecular film is apparently obtained we are in error in our computation of the actual area of the adsorbing material, *i.e.* fissures and capillaries are present in the material, or actual solution of the gas in the adsorbent has taken place; or again, we may consider that multimolecular films may actually exist for certain gases, especially vapours, in the presence of powerful adsorbing agents. In support of this second hypothesis indirect experimental evidence can be advanced from data on the heat of adsorption. For adsorption in multimolecular layers the heat of adsorption falls steadily with increasing quantities of gas adsorbed to a value sensibly equal to the heat of liquefaction.

Thus we note the data of Chappuis on the heat of adsorption of ammonia by meerschaum:

Pressure Range m cm. Hg.	Q cals. per grm.-mol.
0	20,500
0 – 0·5	12,700
0·5 – 3·7	11,300
2·9 – 21	8,970
21 × 57	7,600

Latent heat of liquefaction, L = 5000.

The data of Lamb and Coolidge[2] on the heat of adsorption of vapours of many substances by charcoal in an ice calorimeter show

[1] Langmuir, *Trans. Amer. Inst. Elect. Eng.*, 1921, **32**; Briggs, *J. Phys. Chem.*, 1905, **9**, 617; Katz, *Proc. Amst. Akad.*, 1912, **15**, 445; Pettijohn, *J. Amer. Chem. Soc.*, 1919, **41**, 447; Evans and George, *Proc. Roy. Soc.*, 1923, **103A**, 191.

[2] *J. Amer. Chem. Soc.*, 1920, **42**, 1146.

likewise that the heat evolution per grm. of charcoal q was a logarithm function of the amount adsorbed x:

$$\log q = n + b \log x,$$

and a direct proportionality was not found, as would be the case if a unimolecular layer only was formed.

They likewise indicate a close connection between the heat of liquefaction and the heat of adsorption; whilst the close connection between the amount of gas adsorbed by charcoal and the cohesion of the gas as determined by the a term of Van der Waals' equation, lends additional support to the multimolecular layer hypothesis.

Gas.	$a\ 10^3$.	Adsorbed c.c. per grm. of Charcoal at Standard Pressure.
He . . .	0·42	0·227
Ar . . .	2·59	1·67
N_2 . . .	2·08	2·35
O_2 . . .	2·69	2·50
CO . . .	2·80	3·20
CH_4 . . .	3·67	9·4
CO_2 . . .	7·01	30·4
NH_3 . . .	8·08	73
C_2H_4 . . .	8·83	41

Langmuir[1] in his investigations on the adsorption of carbon monoxide on platinum found that the adsorption isotherm for this gas could not be expressed in the form

$$x = \frac{abp}{1+ap},$$

but in the form

$$x = b + \frac{ab'p}{1+ap},$$

which can most readily be interpreted on the hypothesis that carbon monoxide is very strongly adsorbed for the first layer and that a subsequent layer is adsorbed, obeying the law of the adsorption isotherm. It seems probable that if the adhesive forces between the adsorbent and gas are strong, a factor determined both by the nature of the adsorbent as well as of the gas, that the unimolecular layer will still possess the power of adsorption although more feebly developed. For strong adsorbents dealing with gases which are highly polar in character and near their critical point, layers several molecules thick may readily be imagined to exist. If the gas be below the critical temperature, multimolecular layers can apparently be built up with ease, provided that the pressure be high enough. It may be noted that Hardy's investigations on the effect of substances such as octyl alcohol on the

[1] *Loc cit.*

coefficient of frictions between metal surfaces likewise leads to the conclusion that octyl alcohol when vaporised over a metal surface is adsorbed to form a thick film in which the secondary layers are much less strongly adherent than the primary film.

The question whether a gas can, when it is maintained above the critical temperature, build up a second or more layers on augmentation of the pressure, is as yet uncertain. Indirect experimental evidence for the multimolecular nature of films of vapours adsorbed on solids is provided by the heats of adsorption. But, as we shall have occasion to note subsequently, the surface of the catalyst is by no means uniform in nature, part possessing strong adsorbing powers with other portions of varying activity; a variation in the amounts of different gases adsorbed at what are apparently saturation pressures may indicate, not films of varying thickness, but a covering of varying fractions of the total exposed surface.

We may conclude that at solid as well as at liquid surfaces primary adsorption is accompanied by a marked decrease in free energy. The building up of secondary or multimolecular films is, however, a by no means uncommon phenomenon, especially in the case of vapours on strong or powerful adsorbing agents; whilst the forces operating in the formation of the primary unimolecular film are strong, those in the secondary film are weaker. The primary forces may be compared to the valency forces operative in co-ordination compounds, whilst those in the secondary film are more akin to the cohesional forces operative in vapours and liquids. As an indication of the magnitude of the primary forces may be cited the following data on the average heats of adsorption of gases on metals, these gases in all probability forming but primary films in contact with the metals under consideration:

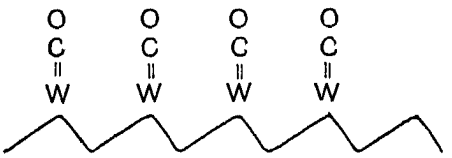
Gas.	Metal.	Q cals. per grm.-mol.
H_2	Pd	18,000 [1]
	Pt	13,760 [1]
	Ni	11,800 [2 3]
	Cu	9,500 [2]
C_2H_4	Ni	5,845 [3]
C_2H_6	Ni	5,000 [3]
CO	Pt	32,000 [4]
	Cu	28,000

A closer investigation of the heats of adsorption of gases reveals an interesting phenomenon, namely, that the heat of adsorption is not a constant value for a particular gas and metal, but is dependent on

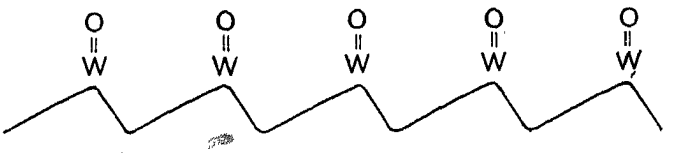
[1] Mond, Ramsay, and Shields, *Zeitsch. physikal. Chem.*, 1898, **25**, 657.
[2] Beebe and Taylor, *J. Amer. Chem. Soc.*, 1924, **46**, 43.
[3] Foresti, *Gazz. Chem. Ital.*, 1923, **53**, 487.
[4] Langmuir, *Trans. Farad. Soc.*, 1921, **17**, 641.

the state of the surface of the metal; highly active metals adsorb gases more readily and possess a higher heat of adsorption. Since, in general, metals prepared at low temperatures possess composite surfaces, the heat of adsorption gradually falls as the more active portions become covered with the gas, resulting in a " spread " of the heat of adsorption. Values ranging from 33,000 to 11,000 calories per grm.-molecule have been obtained for the heat of adsorption of hydrogen on nickel. Similar data are available for carbon monoxide on copper. This " spread " of the heat of adsorption with the pressure is, as we shall note, of importance in attempts to elucidate the nature of the catalyst surface.

Orientation at solid surfaces.—If the indirect measurements of the surface energies of solids are in any way reliable, their surface energies are much greater than for liquids, and it is to be anticipated that adsorption at the surface of solids will result in the formation of a similar layer of orientated molecules. Evidence for this assumption is provided in a number of cases. Langmuir [1] has made an exhaustive study on the adsorption of gases on metallic filaments at low pressures, and has come to the conclusion that definite structural formulæ can be given to the adsorbed layer. Thus, carbon monoxide is strongly adsorbed by tungsten filaments at relatively low temperatures; the union between the carbon monoxide and the tungsten is so great that the whole group (WCO) distils off as a single molecule. At high temperatures, however, the union between metal and gas is by no means so strong, and carbon monoxide is removable unchanged. These experiments, together with the quantitative data on adsorption in a unimolecular layer, lead us to picture a type of adsorption film



Again, small traces of oxygen completely inhibit the action of a hot tungsten wire on the dissociation of hydrogen at high temperatures; the adsorbed oxygen is likewise not reduced by hydrogen, although tungstic oxide is readily reduced. The union of tungsten and oxygen in the adsorbed film must evidently be a very close one, and may perhaps be diagrammatically represented as



The union of these simple gases to metals thus appears similar in nature to a chemical union, which similarity we noted in discussing the data on interfacial surface tension; the data there presented

[1] *Loc. cit.*

indicated that mercury behaved in a similar manner in respect to a decrease in free energy when molecules containing reactive groups are brought in contact with it. There appears little doubt that ethyl iodide, for example, is anchored to the mercury by attachment to the iodine. The investigations of Hardy[1] on the effect of small traces of fatty acids and alcohols on the lubricating properties of a hydrocarbon oil for glass and metal surfaces, indicate also in a striking manner that these organic derivatives are attached by their "polar" $-COOH$ and $-CH_2OH$ groups to these solid surfaces. It may be noted in confirmation of these views that alcohol readily displaces hydrocarbons from the surface of metals such as copper.[2] Similar conclusions as to the orientation of fatty acids on sheets of mica have been arrived at by Sir William Bragg and his co-workers,[3] where it was found that acids allowed to solidify on mica sheets solidified in strata of regular orientated molecules, the direction of orientation being perpendicular to the plane of the mica. Perhaps one of the most convincing pieces of evidence in favour of the hypothesis of orientation on adsorption at the surface of solids is provided by the data of Palmer and Constable on the decomposition rate of a series of primary alcohols at a copper surface according to the reaction $RCH_2OH \longrightarrow RCHO + H_2$. The following data are cited from their experiments :

Catalyst Copper.	Velocity of Decomposition at 205°.	Temperature Coefficients for 10° at 250° C.
I. Ethyl alcohol . .	0·169	1·533
Butyl alcohol . .	0·169	1·543
II. Ethyl alcohol . .	0·258	1·531
Propyl alcohol . .	0·246	1·546

In spite of the marked alteration in the length of the hydrocarbon chain attached to the $-CH_2OH$ group the velocity and temperature coefficient for the alcohols on a specific catalyst are identical, confirming the hypothesis that the $-CH_2OH$ group is the only part of the molecule taking part in the reaction with the copper.

In the above example orientated adsorption occurs in such a manner that the conditions for accelerated reaction are favourable. It is clear that cases may arise, especially in bimolecular surface actions, where the orientation of the adsorbed molecules is such that reaction cannot proceed between the reactive groups. Cases of this character have been investigated by Kruyt and Van Duin;[4] the alkaline saponification of esters and the addition of bromine to sodium p. sulpho cinnamate are retarded by charcoal, although both reactants are adsorbed on the

[1] *Proc. Roy. Soc.*, 1922, **100**, 550; **401A**, 487. [2] Pockels, *Wied. Ann.*, 1899, **17**, 669.
[3] Müller and Shearer, *J. Chem. Soc.*, 1923, **123**, 3156.
[4] *Rec. trav. chim.*, 1921, **40**, 2, 249.

surface. The removal of bromine from $\alpha\beta$ dibromo propionic acid by means of potassium iodide, on the other hand, is accelerated by the presence of charcoal.

Again we shall note that, in discussing the effect of pressure on the velocity of such heterogeneous catalytic actions, we shall be led to considerations as to the "valency" of the adsorption compound formed in the primary layer. Anchoring of the adsorbed molecule may take place on several underlying atoms of the catalyst.

The "availability" of surfaces.—We have noted that Langmuir assumed that the adsorbing surface consisted of a uniform space lattice, each elementary space being the seat of a directive adsorptive force or a potential chemical covalent bond. A more detailed examination, however, reveals the fact that the surface is by no means so uniform as imagined, and that the irregularities are of dominant importance in catalytic reactions. Langmuir himself considered, abstractly, adsorption at a surface non-uniform in character. It is the results of catalytic study which give concreteness to such a consideration.

We must note that the coarse macro-crystalline surfaces are less active than surfaces prepared at low temperatures. If we consider, in the first instance, the chief components of a metal catalytic surface, namely, the edges, corners, and faces of the innumerable small crystals present in the surface, we can draw certain conclusions as to the lack of uniformity, not only in the surface, but also in the surface energy, from crystallographic data. Bravais was the first to note that the planes of a crystal which were most densely packed and were also separated from the neighbouring parallel plane most widely, were those which appeared most frequently, and also that a closely packed surface was usually associated with a wide interplanar distance, and *vice versa*. Later, Gibbs indicated that the most stable planes in a growing crystal were those possessing the least interfacial surface energy.

Although crystal growth rate is markedly affected by such factors as rates of diffusion, local temperature differences, minute alterations in density of the solution, yet, as the investigations of Valeton,[1] Niggli,[2] and Tertsch [3] have indicated, the evidence for a surface energy varying with the closeness of the surface packing is extremely strong. In a similar manner it can readily be shown from a study of the vapour tensions and solubilities of so-called amorphous substances that the atoms at the edges and corners, including those in the corners of the steps on a growing crystal as indicated in the diagram, possess greater

[1] *Phys. Rev.*, 1920, **21**, 106. [2] *Zeitsch. anorg. Chem.*, 1920, **110**, 55.
[3] *Zeitsch. anorg. Chem.*, 1924, **136**, 205.

adhesional force for gases and liquids than atoms situated in the planes of the crystal facets. In addition to this micro-crystalline material present in a metal surface there are present a number of isolated atoms, and groups of atoms which are not in a space lattice and may be designated as amorphous material. These are, as anticipated, even more reactive, as far as adsorption and solution are concerned, than the crystals themselves.

Attention may be directed to the alteration in several physico-chemical properties of materials subjected to extreme subdivision. Thus we have data which indicate that the heats of solution, heats of vaporisation, vapour pressures, dissociation pressures, solubilities of finely comminuted substances, exceed those of the substances in bulk.

This phase is consequently metastable in comparison with the regular crystalline variety, and consequently will slowly revert back to the more closely packed form. In the case of metals the rate of conversion at ordinary temperatures is relatively slow, but on elevation of the temperature these amorphous or irregularly situated atoms readily slip back into the more stable configuration of the space lattice of the element, a process termed sintering. The sintering temperature—*i.e.* the temperature at which the rate of conversion becomes rapid—varies markedly with different metals, and should of course give an approximate value of the energy of the atomic adhesion of the metal. Smith [1] gives the following values for the sintering temperatures of a number of metals:

Metal.	Sintering Temperature ° C.
Pt black	500
Pt ppt.	700
Pd black	600
Ppt Cu	250
Ppt Ni	700
Ppt Ag	180
Au	200
Co	200
Reduced Co	500

Judged by loss of adsorptive capacity of the reduced metal, sintering may take place at much lower temperatures than those recorded by Smith. This loss of adsorptive power is much the most sensitive index of change of surface on heating.[2]

The process of sintering is followed by the growth of the minute crystals to larger ones which become microscopically visible in annealed metals.

Associated with these changes in surface from the unordered and micro-crystalline to the macro-crystalline we find a marked decrease in catalytic activity and in adsorptive power. The following data show the effect of sintering on the adsorption of hydrogen and ethylene on copper and nickel determined by Pease [3] and by Beebe and Taylor: [4]

[1] *J. Chem. Soc.*, 1923, **123**, 2008.
[2] Taylor, 3rd Report on Cont. Cat., *J. Phys. Chem.*, 1924, **28**, 912.
[3] *J. Amer. Chem. Soc.*, 1923, **45**, 1193, 2296. [4] *Ibid.*, 1924, **46**, 43.

Metal.	Temperature of Reduction ° C.	Adsorption of Gas in c.c. per grm. at N.T.P.	
		H_2.	C_2H_4.
Cu . . .	200	3·70	8·45
	450	1·15	6·85
Ni . . .	300	35·0	..
	400	16·0	..

That the surface of a catalyst is composite in character is likewise indicated from the fact that the saturation capacity is not identical for all gases. We have already referred to the fact that many vapours may be adsorbed in multimolecular layers but that in gases unimolecular films are to be expected. Under these conditions the saturation capacity of a catalyst should be identical for all gases ; this is evidently not the case, for, as we note from the figures cited above, ethylene is more strongly adsorbed than hydrogen, and the saturation capacity for the former gas is not reduced so much on sintering.

That this view is probable may be deduced from data on the adsorption of hydrogen by nickel at various temperatures and pressures. From a study of the adsorption isotherms, Gauger and Taylor [1] showed that at relatively low partial pressures of hydrogen an apparent saturation of the surface was reached. Thus at 25° C. and 75 mm. pressure, a given sample of nickel adsorbed 8·7 c.c. of gas. A tenfold increase of pressure did not increase the adsorption by one per cent. At 305° C. apparent saturation was reached at 250 mm. pressure, a threefold increase of pressure not measurably increasing the adsorption. But, at this temperature, the adsorption only amounted to 5·3 c.c. of gas. This spread in the amounts of gas adsorbed at the two temperatures, coupled with the observations made as to the attainment of approximate saturation of the surface, independent of marked pressure increase, is strongly suggestive of the conclusion that the atoms in the surface have varying capacities to hold gas adsorbed, dependent on their position in the surface. It suggests also that a surface atom capable of holding a gas at one temperature may be unable to do so at higher temperature.

It is probable that, on active metals, the "availability" of the surface varies from gas to gas. On the closely packed facets the adsorption forces are, as we have seen, much weaker than on the more open surfaces, and gases which are not readily adsorbed, such as the non-polar, more perfect gases, will not be adsorbed strongly on the crystal facets. On the other hand, polar and easily liquefiable gases will be adsorbed over the entire surface.

This differentiation in the strength of union between adsorbate and adsorbent is also exemplified in the adsorption of oxygen at

[1] *J. Amer. Chem. Soc.*, 1923, **45**, 920.

charcoal and some metal surfaces. It is found, for example, that if oxygen be adsorbed on to a charcoal surface three types of surface compounds can be identified. A small fraction of the oxygen may be removed as such by evacuation, a larger portion may be removed as carbon dioxide by exhaustion at relatively low temperatures, whilst a third more stable portion into which the other forms are gradually converted is only removed at very high temperatures in the form of carbon monoxide and carbon dioxide. Whilst three forms of carbon surface, the diamond, the paraffin or chain, and the ethenoid (to which the black colour is due), are undoubtedly present, the alteration in the type or the strength of union between the superficial and the underlying carbon atoms is reflected in the alteration in the carbon oxygen linkage. Rideal[1] noted that oxygen could be adsorbed on a nickel surface in two forms, one readily reducible by hydrogen at low temperatures, and the other similar to a superficial coating of nickel oxide only reducible at relatively high temperatures. These observations have been extended and confirmed by Larson[2] in the case of copper.

The evidence for a variability in the character of a catalyst surface is provided not only from considerations in respect to crystal structure and the adsorption of gases, but also from experimental data on the rate of catalytic change. Such evidence is provided from two different considerations. We may, on the one hand, calculate the rate of condensation of reactants and rate of evaporation from the catalyst surface with the aid of the Herz-Knudsen equation and a knowledge of the amount of gas adsorbed under the experimental conditions, and compare this theoretical maximum rate of reaction with that actually observed. It will be found that but a minute fraction of the molecules adsorbed on the surface actually undergo chemical reaction; this fraction is found to vary with the nature of the catalyst surface and is not dependent on the energy of activation of the reaction, as is exemplified by the following data of Hinshelwood and Topley[3] on the decomposition of formic acid into carbon dioxide and hydrogen at various surfaces:

Surface.	Energy of Activation. Cals. per mol.	k at 200° C.
Duroglass . .	24,500	$2{\cdot}5\ 10^{-7}$
Gold . . .	23,500	$9{\cdot}2\ 10^{-6}$
Silver . . .	31,000	$1{\cdot}03\ 10^{-5}$
Platinum . .	22,000	$4{\cdot}4\ 10^{-4}$
Rhodium . .	25,000	$2{\cdot}4\ 10^{-3}$
Palladium . .	39,000	$1{\cdot}0\ 10^{-3}$

[1] *J. Chem. Soc.*, 1922, **121**, 318. [2] *J. Amer. Chem. Soc.*, 1925, **47**, 354.
[3] *J. Chem. Soc.*, 1923, **123**, 1014.

Evidently the catalytically active patches are greater in extent on the metals of the platinum series than on silver and gold or duroglass, whilst the energies of activation are all comparable, with the exception of palladium.

Again, we find that on the addition of minute amounts of poisons to catalysts a very serious reduction in the reaction velocity occurs without any sensible diminution in the adsorption of the reactants taking place. Many cases of qualitative fractional and selective poisoning will be discussed in a subsequent section. A few quantitative experiments have been made on the relative areas of patches of varying activity; thus Rideal [1] found that 0·01 per cent only of a nickel surface was effective in catalysing the union of hydrogen and ethylene. Pease [2] noted that but a few cubic millimetres of carbon monoxide poisoned a copper surface for the same reaction. Rideal and Wright [3] found that on an active sugar charcoal 0·04 per cent of the surface was autoxidisable and 40 per cent of the surface was catalytically active.

Recent experiments by Richardson [4] on thermionic emission from metal surfaces have revealed the interesting fact that electron emission from a hot surface does not occur uniformly over the surface but apparently from localised patches. It is an interesting speculation to associate these patches which are thermionically active with the active patches identifiable by adsorption and catalytic means.

That some connection may exist is evident from the experiments of Thompson,[5] who showed that thermionic emission commenced from a platinum wire when raised to the temperature at which the union of hydrogen and oxygen on the surface commenced. Langmuir [6] likewise noted that when sufficient poison had been admitted to a reacting system containing a catalytic tungsten wire to suppress the catalysis, thermionic emission was simultaneously suppressed.

Activation of metal surfaces.—In the foregoing sections we have discussed somewhat briefly the evidence in favour of the hypothesis that catalysis occurs on localised reaction centres which may be relatively small in area compared to the total surface exposed to the reactants. These localised reaction centres are characterised by strong adsorbing powers, as is exemplified by the behaviour of traces of poisons on the reaction velocity; whilst these in turn are related to the configuration of the metal surface, an open packing or irregular atomic distribution being more effective than a closely packed surface. These conclusions throw light on the process of activation of a metal surface. It is well known that repeated alternate oxidations and reduction at low temperatures render metals such as copper, iron, and nickel extremely active. An investigation on the increase in

[1] *Loc. cit.*
[2] *J. Amer. Chem. Soc.*, 1923, **45**, 1193, 2296.
[3] *J. Chem. Soc.*, 1925, **127**, 1347.
[4] *Proc. Roy. Soc.*, 1925, **107A**, 377.
[5] *Physikal. Zeitsch.*, 1913, **14**, 11.
[6] *Loc. cit.*

catalytic activity of copper for the dehydrogenation of ethyl alcohol after a series of oxidations and reductions at 250° C. showed that if precipitated copper oxide were utilised as source of copper a marked increase in catalytic activity was to be observed after two reduction processes had been completed, subsequent oxidations and reductions scarcely affecting the catalytic activity. In the first reduction copper is formed from cupric oxide, and a skeleton of metal pseudomorphic with the original copper oxide results. Dunn[1] has shown that this "open" variety of copper is stable up to 400° C.; at higher temperatures it commences to sinter and reverts back to the more closely packed configuration of metallic copper, with a corresponding reduction in permeability to gases and catalytic activity. On the second oxidation, cuprous oxide is formed which, on reduction, yields an even more open network of copper. Subsequent oxidations and reductions do not open the lattice any further, and it has been noted that even a small decrease in catalytic activity may occur, due to collapse of the open structure. This artificial increase in the relative area of active surface must be distinguished from an increase in the total surface area by artificial means, an increase which may be associated with a relative decrease in the fraction of surface catalytically active, a point which we shall have occasion to discuss in a subsequent section.

The reaction velocity of catalytic changes.—In the preceding sections arguments have been advanced in support of the hypothesis that molecules adsorbed in the primary film are orientated and held relatively firmly. Such adsorption is orientated, since particular groups in complex molecules affect the values of the adhesional forces. In addition we have noted that only a small fraction of the surface even of an active material is catalytically effective.

Bodenstein[2] and Bodenstein and Stock[3] assumed that reaction proceeded in the adsorbed gas layer around the catalytic material which served merely to condense the gas in an atmosphere around the surface. The reaction velocity, on this view, was governed by the rate of diffusion of reactants or products through this adsorbed thick film, the thickness of which was a function of the pressure. This point of view was shown to be untenable by Langmuir[4] for heterogeneous gaseous reactions, but, as we shall note, limitations due to rates of diffusion frequently play an important part in heterogeneous reactions in liquids.

It is found, for example, that the decomposition rate of certain hydrides is materially affected by the pressure of the gas, as is evident from the following data.

According to Bodenstein's view the film thickness should be proportional to the pressure for phosphine and arsine, and proportional to the square root of the pressure for hydrogen and ammonia.

[1] Unpublished experiments.
[2] *Zeitsch. physikal. Chem.*, 1899, **29**, 665.
[3] *Ber.*, 1907, **40**, 570.
[4] *J. Amer. Chem. Soc.*, 1916, **38**, 2289.

Gas.	Surface.	Reaction Rate.	Investigator.
H_2	Tungsten	$\frac{dx}{dt}=K\sqrt{P}$	Langmuir, *loc. cit.*
PH_3	Phosphorus	$\frac{dx}{dt}=KP$	Koos, *Zeitsch. physikal. Chem.*, 1893, **12**, 155. Trautz, *Zeitsch. anorg. Chem.*, 1919, **106**, 95
AsH_3	Arsenic	$\frac{dx}{dt}=KP$	Cohen, *Zeitsch. physikal. Chem.*, 1896, **20**, 303 ; 1898, **25**, 483
SbH_3	Antimony	$\frac{dx}{dt}=KP^{0.6}$	Stock, *Ber.*, 1918, **41**, 1319
NH_3	Quartz glass	$\frac{dx}{dt}=K\sqrt{P}$	Bodenstein, *Ber.*, 1907, **40**, 570

Langmuir showed, from a consideration of the observed reaction velocity and the rate of condensation of the gas on the catalyst surface, that " the velocity is in general not fast enough materially to affect the equilibrium between the adsorbed film and the surrounding gas ". We must imagine that in such reactions molecules are continually hitting the surface, condensing there, and after a time interval more or less short either evaporating unchanged or undergoing decomposition with subsequent evaporation of the reaction products. Before attempting to analyse in more detail the mechanism by which a condensed molecule selectively re-evaporates unchanged or undergoes surface decomposition, we find that Langmuir's point of view affords valuable evidence as to the structure of the adsorption compound that is formed on condensation of the reactant. This evidence, together with the inference as to the points of attachment derived from the considerations previously advanced, gives us a relatively good picture of the structure of the surface compound. In the case of the surface catalytic decompositions referred to above, there are evidently two extremes : either the surface, *by which is meant the catalytically active surface*, is covered only to a small extent with the reacting gas, or it may be almost completely covered.

In the first case we may, on analogy with our previous considerations (p. 35), write

$$\text{Rate of condensation of unchanged gas} = \alpha\mu ;$$
$$\text{Rate of evaporation of unchanged gas} = \nu_1\theta^n,$$

where n represents the number of elementary spaces on the surface occupied by each molecule of the reactant and θ is the fraction of surface covered.

The product of chemical reaction is formed by the combination of molecules from m adjacent spaces.

If $\frac{dx}{dt}$ represents the velocity of chemical change,

$$\frac{dx}{dt}=\nu_2\theta^m.$$

Hence $$\frac{dx}{dt}=\nu_2\left(\frac{a\mu}{\nu_1}\right)^{\frac{m}{n}}.$$

The velocity thus varies as the m/n power of the gas pressure. In the case of the dissociation of hydrogen on tungsten Langmuir found $\frac{m}{n}=\frac{1}{2}$; whilst for the recombination of hydrogen atoms on tungsten he found $\frac{m}{n}=2$. These relationships are at once intelligible if it be assumed that a hydrogen atom occupies or is attached to but one elementary space on the lattice; the hydrogen molecule would thus occupy two spaces. Whilst absolute values cannot be assigned to m or n in such cases as in the decomposition of the hydrides, it is clear that in cases such as the decomposition of phosphine where $m=n$, diagrammatic representation is possible by assigning a value of $m=n=2$ for the reaction.

On this view of valency of adsorption compounds, stibnine, which at low temperatures possesses an exponent of 0·6, must be assumed to undergo a composite reaction, for it is clear that m/n must be some simple fraction or integer. This is confirmed by the fact that the exponent rises to unity with elevation of the temperature. It is possible that stibnine undergoes two types of surface reaction, one similar to that of ammonia on quartz glass, and the other comparable to that of arsine, the latter predominating at high temperatures.

We have noted that there exists another case of simple decomposition at a catalytic surface in which the surface is completely covered. Under these conditions the surface concentration will be constant and independent of the pressure; thus, the reaction velocity will be independent of the pressure and depend only on the extent of catalytically active surface. A number of reactions of such a type corresponding to a reaction of zero order have been examined, such as the decomposition of alcohols at a copper surface and the decomposition of formic acid at solid surfaces.

Multimolecular surface actions.—Similar considerations may be applied to the more complicated interactions, catalytically accelerated at solid surfaces. A number of these have been examined in detail, such as the oxidation of sulphur dioxide to trioxide at the surface of platinum,[1] the oxidation of carbon monoxide at the surface of quartz [2] and of platinum,[3] and the hydrogenation of ethylene at nickel surfaces,[4] and also at copper surfaces.[5]

[1] Bodenstein and Fink, *Zeitsch. physikal. Chem.*, 1917, **60**, 1.
[2] Bodenstein and Ohlmer, *ibid.*, 1905, **53**, 175.
[3] Langmuir, *J. Amer. Chem. Soc.*, 1915, **37**, 1162; *Trans. Farad. Soc.*, 1921, **17**, 621.
[4] Palmer, *Proc. Roy. Soc.*, 1921, **99A**, 402; Rideal, *J. Chem. Soc.*, 1922, **39**, 309.
[5] Pease, *J. Amer. Chem. Soc.*, 1923, **45**, 1193, 226.

For the oxidation of carbon monoxide Bodenstein and Ohlmer found e following reaction velocities :

(*a*) On crystalline quartz $\frac{dx}{dt} = K P_{CO} \sqrt{P_{O_2}}$.

(*b*) On quartz glass $\frac{dx}{dt} = \frac{K' P_{O_2}}{P_{CO}}$.

we assume that on crystalline quartz the carbon monoxide occupies .e elementary space on the lattice, we obtain for the conditions of uilibrium

$$\alpha_1 \mu_1 = K_1 \theta_1.$$

)r the oxygen which we assume occupies two elementary spaces,

$$\alpha_2 \mu_2 = K_2 \theta_2^2.$$

eaction takes place between adjoining carbon monoxide molecules .d oxygen atoms, or

$$\frac{dx}{dt} = k_3 \theta_1 \theta_2$$
$$= K P_{CO} \sqrt{P_{O_2}}.$$

1 quartz glass, on the other hand, the adsorptive forces are apparently ronger at the localised active patches, and we must assume that these tches are almost completely covered with an adsorbed film of carbon onoxide. The rate of condensation of this gas will be

$$\alpha_1 \mu_1 \theta,$$

d since θ is small and constant we obtain

$$\alpha_1 \mu_1 \theta = k_1.$$

ıe oxygen undergoes reaction when its molecules come into contact th the uncovered surface; thus the rate of reaction will be

$$\frac{dx}{dt} = k_2 \theta \mu_2$$
$$= k_2 \mu_2 \left(\frac{k_1}{\alpha_1 \mu_1} \right) = K \frac{P_{O_2}}{P_{CO}}.$$

In addition to these simple cases many more complicated examples ıve been worked out on the general principles laid down by Langmuir. ttention may be drawn to three phenomena occurring in such surface actions, which appear to be by no means uncommon.

(*a*) *Reaction by contact with an adsorbed molecule or atom.*— ıngmuir [1] has shown that carbon monoxide undergoes oxidation at platinum surface chiefly by striking atoms already present on the ırface as a result of adsorption of oxygen molecules on two elementary

[1] *Loc. cit.*

spaces. There is some new evidence obtained by Wolfenden[1] which indicates that some hydrogenation processes occur by collision of reactants with hydrogen atoms present on a metal surface, though it seems also that not all hydrogenation processes may be so achieved.[2]

(*b*) *Inhibition by reactants.*—We have noted that the *general* equation for a reaction between two gases on a surface which does not adsorb either reactant very strongly can be expressed in the form

$$\frac{dx}{dt}=K\theta_1^{n}\theta_2^{m},$$

where θ_1, θ_2 represent the fractions of the active surface covered by the respective n and m valent reactants.

If the surface be almost completely covered with both reactants

$$\theta_1+\theta_2=1,$$

whence

$$\frac{dx}{dt}=K\theta_1^{n}(1-\theta_1)^{m}.$$

Thus, the reaction velocity will be at an optimum for a particular ratio of the reacting gas pressures sinking on either side of this optimum as the ratio of the reactants is increased or decreased. The existence of this optimum has been shown for ethylene and hydrogen at a copper surface by Pease, at a nickel surface by Rideal, and at a charcoal surface in the oxidation of oxalic acid by Rideal and Wright.

(*c*) *Inhibition by the reaction products.*—In the case of the hydrogenation of ethylene the ethane produced does not exert any inhibiting action, but many cases are to be found in which the reaction products are strongly adsorbed and thus slow down the reaction velocity. Thus, Bodenstein and Fink noted the inhibiting action of sulphur trioxide on the oxidation process of the dioxide at the surface of platinum, Burk and Hinshelwood[3] that of hydrogen in the decomposition of ammonia, and Hinshelwood and Pritchard[4] of oxygen on the decomposition of nitrous oxide at platinum surfaces.

We may divide these cases into two classes, those in which the reaction product is very strongly adsorbed, and those in which it is adsorbed relatively as strongly as the reactants. As an example of the former we may take the case of the oxidation of sulphur dioxide. We may imagine the catalyst surface covered with a layer of SO_3 molecules each occupying two elementary spaces.

The rate of condensation will be $\alpha\mu\theta^2$ and the rate of evaporation ν will be constant, since the surface is nearly completely covered.

Since equilibrium obtains

$$\nu=\alpha\mu\theta^2.$$

In the presence of excess oxygen any vacant spaces on the active

[1] *Proc. Roy. Soc.*, 1926, **110A**, 465.
[2] Taylor and Marshall, *J. Phys. Chem.*, 1925, **29**, 1140.
[3] *J. Chem. Soc.*, 1925, **127**, 1105.
[4] *J. Chem. Soc.*, 1925, **127**, 331.

catalyst will be occupied by this gas, and the sulphur dioxide enters into reaction when it strikes the space occupied by the oxygen at a rate proportional to $\theta\mu_{SO_2}$. Hence we obtain

$$\frac{dx}{dt}=\nu_2(\theta\mu_{SO_2})=\nu_2\mu_{SO_2}\sqrt{\frac{\nu}{\alpha\mu}}=K\frac{P_{SO_2}}{\sqrt{P_{SO_3}}}.$$

In the presence of excess sulphur dioxide the reaction velocity will evidently be $\frac{dx}{dt}=K\frac{P_{O_2}}{\sqrt{P_{SO_3}}}$, in agreement with the experimental data of Bodenstein and Fink.

In the decomposition of nitrous oxide at a platinum surface, according to the equation

$$2N_2O \longrightarrow 2N_2+O_2,$$

Hinshelwood and Pritchard[1] found that oxygen exerted a retarding influence. If θ be the fraction of the active surface covered with the oxygen film at equilibrium, the rate of condensation and evaporation will be equal, or

$$\alpha\mu(1-\theta)=\nu\theta,$$

whence

$$1-\theta=\frac{\nu}{\nu+\alpha\mu}=\frac{1}{1+b(O_2)}.$$

The rate of decomposition of nitrous oxide on the bare catalytic surface will be accordingly

$$-\frac{dN_2O}{dt}=k(N_2O)(1-\theta) \text{ or } \frac{kN_2O}{1+b(O_2)},$$

or

$$\frac{dx}{dt}=\frac{K(a-x)}{1+bx},$$

where a is the original pressure of the nitrous oxide. The agreement between the observed values and those calculated with the aid of the above equation is shown in the following table:

P_{O_2}.	$\frac{dx}{dt}$ calc.	$\frac{dx}{dt}$ observed.
23	46	44
40	35	36
745	29	26
112	20	20
159	14	15
206	10	12·5
257	10	10·4
305	10	9

[1] *J. Chem. Soc.*, 1925, **127**, 331.

The reaction velocity in solutions.—In the case of heterogeneous catalytic gas reactions we have noted that the diffusion hypothesis of Faraday and Bodenstein could in general not be substantiated. In all cases yet examined the observed surface reaction velocities are much smaller than the rate of contact of the gaseous reactants. In solutions, however, and possibly also in cases where the surface reaction velocities are high, such as in the cases of surface combustion examined by Bone, the rates of diffusion may be comparable to the rate of chemical action. It is clear that if the rate of diffusion be the limiting factor in such action, the influence of temperature on the reaction velocity will be that corresponding to the temperature coefficient of diffusion, which is small in gaseous and liquid media.

Zero order reactions.—It has already been observed that in many heterogeneous gas reactions, such as the decomposition of alcohols and esters at the surfaces of metals and metallic oxides, the rate of decomposition is independent of the pressure, an experimental fact readily intelligible on the assumption that the reactants are strongly adsorbed and that the reaction velocity actually measured is the rate of conversion of the adsorbed reactants and subsequent evaporation of the products. At sufficiently low pressures a departure from zero order reaction is to be anticipated. Such zero order reactions are frequent in liquid systems. We find, for example, that many enzyme reactions such as the hydrolysis of sugars as observed by Armstrong,[1] Hudson[2] and Nelson,[3] obey within wide limits such a law (see also Chap. XIII.).

The case of the hydrogenation of unsaturated organic substances at colloidal and massive nickel and platinum surfaces presents some interesting features. The reaction velocity of hydrogenation has been studied with a view to elucidation of the mechanism by a number of investigators, notably Paal,[4] Fokin,[5] Ubblehode and Svanoe,[6] Thomas,[7] Rideal,[8] Armstrong and Hilditch.[9] One of the factors unconnected with the mechanism of the reaction is the rate of supply of hydrogen by diffusion through the liquid to the catalyst surface. It is found that this rate of supply is augmented by agitation, the rate of hydrogenation is determined over a limited range by the agitation rate n, and the relationship

$$\frac{dx}{dt} = Kn^2$$

is obeyed.

A similar dependence of reaction velocity on the agitation rate was noted by Bredig and Teletow[10] in the decomposition of hydrogen

[1] *Proc. Roy. Soc.*, 1924, **73**, 500.
[2] *J. Amer. Chem. Soc.*, 1908, **30**, 1160, 1564.
[3] *Ibid.*, 1916, **38**, 1109.
[4] *Ber.*, 1907, **40**, 2309; 1908, **41**, 805.
[5] *Zeitsch. angew. Chem.*, 1908, **22**, 1451, 1492.
[6] *Ibid.*, 1919, **32**, 257, 276.
[7] *J. Chem. Soc. Inst.*, 1920, **39**, 120.
[8] *Trans. Farad. Soc.*, 1923, **19**, 1.
[9] *Proc. Roy. Soc.*, 1919, **96A**, 137; 1920, **98A**, 27; 1921, **100A**, 240.
[10] *Zeitsch. Elektrochem.*, 1906, **12**, 581.

peroxide at a platinum surface. In this case a limitation to the rate of reaction is set by the rate of diffusion of hydrogen peroxide through the "diffusion layer" [1] of water adhering to the platinum, the thickness of this layer being reduced under increased agitation. Above certain critical speeds, however, it is found that the rate of hydrogenation as well as the rate of decomposition of hydrogen peroxide is unaffected by the rotation speed, and the rate is thus not influenced by the rate of supply of hydrogen to the catalyst. An examination of the hydrogen uptake time curves indicates that with pure materials and active catalyst the curves are linear in character until the reaction is nearly completed, when a unimolecular form appears. With old and feebly active catalysts the zero order portion of the curve becomes smaller and the curve over an extended period of time acquires a unimolecular character. It has also been shown in the case of sodium cinnamate and sodium phenyl propriolate that these reactants are strongly adsorbed by a colloidal palladium catalyst. It appears that the rate of reaction in the hydrogenation of pure substances is proportional to the concentration of a ternary complex hydrogen-unsaturated compound-catalyst, similar to the many bimolecular surface gas reactions already discussed.

For organic substances strongly adsorbed at the catalyst surface the surface concentration will be independent of the bulk concentration; for substances feebly adsorbed and on inactive catalysts the surface concentration will be related to the bulk concentration by an equation of the Freundlich or Langmuir type. The reaction velocity will thus be independent of the bulk concentration until this falls to such a value that the surface concentration suffers a diminution. Poisoning by reaction products, gradual adsorption of poison from the reaction mixture, accumulation of impurities in the hydrogen, and other similar disturbances, readily cause a departure from the linear type of curve.

Uni- and pseudo-unimolecular reactions. — Whilst over a large portion of the curve the reaction velocity of hydrogenation is of zero order with respect to the substance undergoing hydrogenation, the effects of variation of hydrogen pressure are by no means so definite. If the adsorption complex nickel-organic substance is relatively stable it is clear that, as in the ethylene hydrogen combination (Rideal and Pease), the reaction velocity should be proportional to the hydrogen pressure, a conclusion verified experimentally in simple cases by Armstrong and Hilditch. For low concentrations of catalyst the increase in rate is less than proportional to the increase in pressure, whilst it was found that if the unsaturated compound contained a group which had an affinity for nickel but was not open to hydrogenation, an increase in hydrogen pressure caused a more than corresponding increase in reaction velocity. The decomposition of

[1] See Noyes and Whitney, *Zeitsch. physikal. Chem.*, 1897, **23**, 689; Brunner, *ibid.*, 1900, **35**, 283; Nernst, *ibid.*, 1904, **47**, 52.

hydrogen peroxide at the surface of massive platinum is, as we have noted, limited over a certain range of speed of agitation by the rate of diffusion of the hydrogen peroxide through the diffusion layer, and is thus pseudo-unimolecular in character.

At the surface of colloidal metals and oxides such as platinum, manganese dioxide, cobaltic oxide, and copper oxide, Bredig and his co-workers [1] obtained an approximately unimolecular rate of decomposition in slightly alkaline solution. There is, however, a relative increase in the velocity constant as the reaction proceeds, and, in addition, the temperature coefficient is relatively high (*ca.* 2·4 for 10° C. rise). These two facts cast doubt upon the hypothesis that the pseudo-unimolecular character of the reaction velocity is a measure of the diffusion rate of hydrogen peroxide through the diffusion layer. It is more than probable that but a small portion of the colloidal particles are catalytically active, and that we are measuring the true rate of chemical reaction at the surface. The phenomena associated with colloidal catalysts receive a more detailed consideration in a subsequent chapter (Chap. XIII.).

There are many other examples of catalytic acceleration by massive and colloidal platinum to be noted in aqueous solutions. Thus, a number of ionic oxidations are accelerated by the metal; *e.g.*:

$Ti''' + \dot{H} \longrightarrow Ti^{IV} + H$	Diethelm and Förster, *Zeitsch. physikal. Chem.*, 1908, **62**, 129.
$Co_2(CN)_6^{IV} + \dot{H} \longrightarrow Co(CN)_6''' + H$	Denham, *ibid.*, 1910, **72**, 641.
	Manchot and Herzog, *Ber. Chem. Ges.*, 1900, **33**, 1742.
$Cr'' + \dot{H} \longrightarrow Cr''' + H$	Jablczynski, *Zeitsch. physikal. Chem.*, 1908, **64**, 748.

Whether these reactions are limited in respect to their velocity by diffusion or the specific surface chemical reaction rate, requires further investigation. It is more than probable that the transition from one limitation to the other on agitation of the liquid, as noted in the case of hydrogen peroxide, may be obtained in these cases also.

The energy of excitation.—In the case of bimolecular gaseous reactions we have noted the necessity for adopting the hypothesis of active or excited molecules, the energy of activation or excitation being provided by inelastic collision. For heterogeneous reactions likewise a similar hypothesis is necessary, for a simple calculation indicates that but a small fraction of the molecules of a gas impinging on an active catalytic surface actually suffers decomposition. We have noted that many such actions proceed with uniform velocity although the pressure of the gas or concentration of the reactant in solution may undergo wide variations, and it is inferred that the

[1] *Zeitsch. physikal. Chem.*, 1899, **31**, 258; 1901, **37**, 1; *Ber.*, 1904, **37**, 798.

catalytic surface is strongly adsorbent. Thus, the increase in velocity of the reaction on elevation of the temperature will, as we shall note, for these reactions, be almost a true measure of the critical energy increment. In many reactions, the active surface may undergo alteration in area on elevation of the temperature; thus, poisons may be partially desorbed with consequent increase in active area; the temperature coefficient will in these cases be abnormally large. Again, the configuration of the surface of a sensitive catalyst may alter as the temperature is raised, due to the increased rate of sintering. In the case of heterogeneous bimolecular reactions, inferences from the temperature coefficient of the reaction are liable to be misleading; thus, if one reactant be strongly adsorbed and the other undergoes reaction when it strikes a vacant space on the catalyst surface, the temperature coefficient will yield merely a measure of the latent heat of adsorption of the strongly adsorbed reactant.

For simple surface reactions, however, proceeding under conditions so that the surface is always saturated, the calculation of the energy of excitation yields approximately correct values. In the cases fulfilling these conditions, which have been examined with care, it is found that the energy of excitation of the catalysed reaction is always less than that of the uncatalysed homogeneous bimolecular gas reaction.

Thus, in the decomposition of nitrous oxide, which occurs both as a bimolecular homogeneous gas reaction and on the surface of platinum, Hinshelwood and Pritchard [1] found for the homogeneous reaction both from the temperature coefficient and from the relationship

$$\frac{\text{Number of effective collisions}}{\text{Total number of collisions}} = e^{-\frac{E}{RT}},$$

a value of $E = 55{,}000$ cals., whilst from the temperature coefficient of the surface reaction a critical energy increment of 32,500 calories per grm.-mol. was found. Rideal and Norrish [2] found for the homogeneous gas reaction $H_2 + \frac{1}{2}S_2 = H_2S$, a critical increment of 51,460 cals.; for the surface action between hydrogen and sulphur, a value of 25,750 cals.

Hinshelwood has pointed out that in the case of simple decomposition of N_2O, HI, and Cl_2O, for the surface reaction the activation of one molecule takes place, but, in the bimolecular gas reaction, the critical energy increment to be supplied must be sufficient to activate two molecules of the reacting species. The acceleration produced by such a conversion from a bimolecular to a "unimolecular" reaction is thus clearly intelligible, although the actual energy of excitation per gram-molecule may be very similar in the two cases.

In the case of homogeneous bimolecular reactions the energy of excitation is supplied by collision between the molecules. It might

[1] *J. Chem. Soc.*, 1925, **127**, 330. [2] *J. Chem. Soc.*, 1923, **123**, 3216.

be suggested that only those molecules hitting the active catalyst surface with kinetic energy equal to or in excess of the critical value undergo activation and decomposition, the remainder merely condensing and undergoing subsequent evaporation.

There are, however, several alternative possibilities which cannot lightly be dismissed. Thus, we may consider that an adsorption compound is first formed between catalyst and reactant, and that this compound is subsequently supplied with activating energy by collision or by radiation. Again, the actual act of adsorption may result in the production of an activated species. The kinetic energy of the accompanying molecule, the surface energy of the catalyst, and the change in internal energy of the surface and adsorbate consequent on the formation of the surface complex, may all contribute to such activation. The specificity and localised activity of catalysts, as well as the extreme rapidity with which the kinetic energy of a colliding molecule is damped on collision with a solid surface (Langmuir), favour the view that the activation occurs in the catalyst-gas complex.

The relationship between evaporation and decomposition of an adsorbed molecule may be suggestively considered in the following manner. The number of molecules evaporating per second per unit area of active surface at a temperature T may be written, if such surface be covered at all temperatures,

$$N\nu e^{-\frac{Q}{RT}},$$

where N is the number adsorbed and $\frac{1}{\nu}$ the mean life of an adsorbed molecule after activation with a quantity of energy Q, the latent heat of evaporation. The number of molecules per unit area of active surface undergoing decomposition per second will be

$$N\nu' e^{-\frac{E}{RT}},$$

where $\frac{1}{\nu'}$ is the mean life of a molecule after activation with E, the critical energy increment for decomposition.

The mean lives $\frac{1}{\nu}$ and $\frac{1}{\nu'}$ of the complexes between excitation and evaporation or disintegration correspond to Maxwell's period of molecular relaxation, since not only are vacant spaces filled up immediately, but the adsorbed molecules may be regarded as akin to a two-dimensional gas possessing purely vibrational energy in one vertical plane. The time of molecular relaxation in a homogeneous gas is $\frac{1}{\eta\Delta}$, where η is the viscosity and Δ the density, and thus varies but slowly with the temperature. Since the process of readjustment of the distribution of energy in the surface phase after evaporation or dis-

tegration is the same, it is probable that the mean lives are extremely ort and possibly related to Q and E by the relationship $Q = Nh\nu'$, $= Nh\nu'$, as suggested on p. 44.

Even more complex are cases such as the decomposition of alcohols, ters, and formic acid, the surface compounds of which may undergo aporation, and two different types of surface decomposition each th its own characteristic critical energy increment for the particular talyst employed. The fact that the rates of the two modes of composition are in no way related to the critical energy increments clearly in favour of the hypothesis that we are dealing with two rface compounds of different character and structure, each of which ay undergo the evaporation change but only one form of decom- sition. It is to be anticipated that the heats of adsorption to form ese two species of compounds would be different, and the hypothesis the existence of these two types might thus receive experimental nfirmation.

Apparatus employed.—The most important heterogeneous catalytic actions include those in which the reactants are forced through a bed granular contact material, the effluent gases or liquids being then bmitted to analysis. Many examples of such reactions are to be und in technical practice, such as the catalytic process for the eparation of ammonia, hydrogen from water gas, the removal of lcium and magnesium salts from hard waters by sodium zeolites chlorine from hydrochloric acid. The advance to be recorded in e scientific investigation of the hydrodynamics of the problem is t considerable.

It is at once evident that if a volume V of reactants be passed rough a volume v of material per hour, the "space velocity" or e volume of gas passed through unit volume of catalyst is $\frac{V}{v}$ litres r c.c.) per litre (or c.c.) per hour. The "space velocity" (or S.V.) an important characteristic, especially for technical purposes, and clear statement of the space velocity is necessary when the feasibility any process is under discussion. A closer analysis of this definition ll, however, indicate that there is some uncertainty about the details this conception. It must be understood that the S.V. (space locity) is always referred to the reactants at normal temperature d pressure, a matter of considerable importance when the reaction kes place in the vapour or gaseous state at elevated temperatures. gain, the conception of "reactant" permits of a certain degree of titude. Thus, in the synthesis of ammonia from nitrogen and drogen in the stoichiometric ratios 1 : 3 both the gaseous con- ituents take part in the reaction, and since the stoichiometric relations e not altered after catalysis, both gases are to be considered as actants. In other cases, such as in processes of hydrogenation, of lective combustion, or of the conversion of water gas into hydrogen

and carbon dioxide in the presence of steam, the question arises as to whether the S.V. should be referred entirely to the reactant, *i.e.* the substance undergoing hydrogenation or combustion, or again to the carbon monoxide in the water gas. Thus, in the case of the water-gas conversion, the quantity of hydrogen in the gas or of steam employed might conceivably modify profoundly the velocity of reaction at the surface of the catalyst.

The procedure generally adopted is to refer the S.V. to some important constituent of the reactants. Thus, in the water-gas reaction, the S.V. may be taken from the mean of the total volume of gas entering and leaving the catalyst mass corrected to N.T.P. after condensation of the steam, whilst in cases of hydrogenation of, say, an oil, the S.V. would be referred to the mass of oil hydrogenated per unit volume of catalyst space or per unit mass of catalyst.

From the space velocity a second figure, no less important for technical operations, may be obtained, namely, the "space time yield" (or S.T.Y.). If the fractional conversion of reactants accomplished by a single passage through the catalyst mass at a space velocity of V be R, then the space time yield or the yield in litres of desired product per litre of catalyst space per hour will be RV. In many cases, for convenience, the S.T.Y. is expressed in kilograms per litre of catalyst space per hour, or other similar units which give a numerical value to the product RV.

It may be observed that there is a relationship between R and V, since for low values of V the equilibrium under the conditions of operation is arrived at and R attains its maximum value. With an increase in the space velocity, equilibrium amongst the reactants may not have time to establish itself during the passage through the contact mass, and with exceedingly high space velocities the composition of the reactants will scarcely be affected by such passage. Thus, to attain a maximum value of the product RV, it is not necessarily or indeed always desirable to limit the space velocity to such low figures as may be necessary to ensure attainment of equilibrium. Higher values for the S.V. and a lower conversion may give a greater output per hour. The RV, V curve will consequently assume some such form as the diagram (Fig. 4).

(i.) The region O to a, in which equilibrium is established at all velocities up to a space velocity of a', whence the product RV is proportional to V. (ii.) The region a to b, where from space velocities a' to b' equilibrium is not established and the percentage conversion gradually falls off, the product RV increasing, however, with increasing values of V. (iii.) The region b to c, where, with exceedingly high space velocities, the rate of diminution of R, the fractional conversion, exceeds the rate of increase in the space velocity, with a consequent decrease in hourly output.

In all circulating processes the optimum space velocity is repre-

sented by the point b' on the characteristic $R\,V$, V curve, whilst for non-circulating processes the maximum hourly output and the best utilisation of the reactants (in those cases where equilibrium conditions are desired) is attained at space velocities indicated by the point a'.

No satisfactory data have been published on the design of converters for such types of heterogeneous catalysis, but the following points which bear upon this subject may be mentioned.

We have derived a figure for the space velocity from a consideration of the rate of flow of the reactants through a given volume of catalyst space. This figure evidently gives us no information as to the actual velocity through that space, since part is occupied by the catalytic

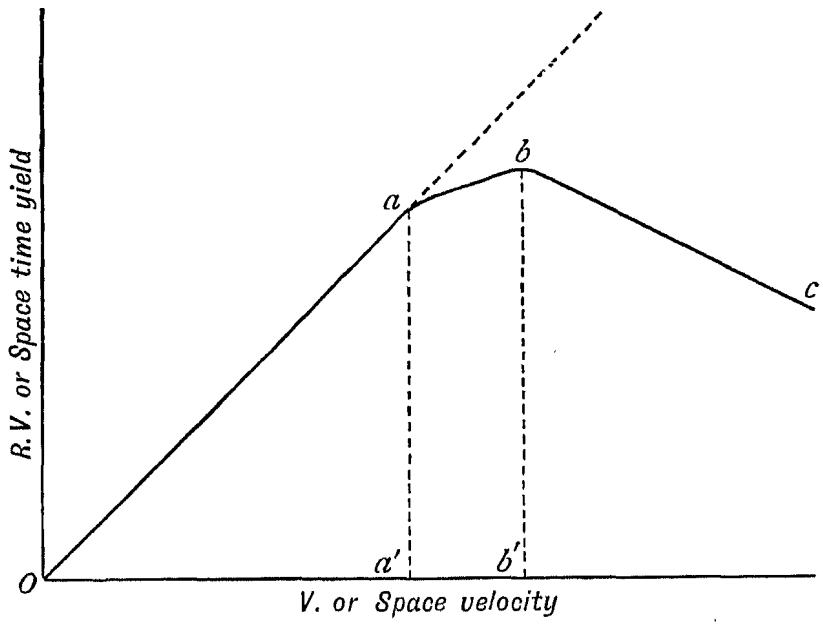


FIG. 4.

material. For purposes of calculation we may assume that the catalyst consists of a number of uniform spheres, and, further, that they are packed in a simple and regular manner in the catalyst chamber.

It can be easily shown, for the simplest type of spherical packing, viz. point contact in sets of three, thus :

that the free space unoccupied by the spheres (assumed inelastic and incompressible) is 33·5 per cent of the total volume occupied and is independent of the diameter of the spheres, whilst the free cross-sectional area is 9·55 per cent of the area of the catalyst chamber and is likewise independent of the diameter of the spheres. The dependence of the area of contact exposed by the surface of the spheres on the

diameter of the individual is exemplified in the following curve (Fig. 5). The advantages of fine packing are clearly demonstrated.

The works of O. Reynolds on gravitational theory, and of Pope and Barlow on chemical crystallography, may be consulted for other types of spherical packing. They will be of use in giving an orientation into the problems of arrangement of the catalyst bed, but their utility is limited by the deviations of the catalytic material from spherical shape.

It is evident that for a S.V. of V the true space velocity is approximately $3V$, when due allowance is made for the space occupied by the catalytic material, and that the linear velocity in metres per

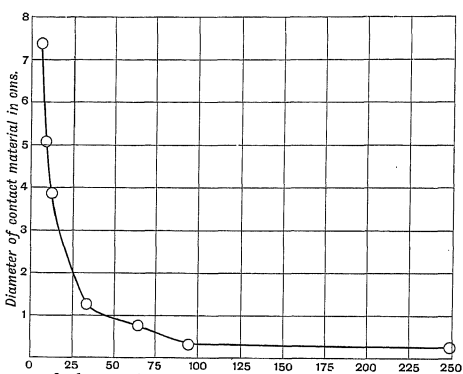


FIG. 5

second may be obtained by calculating the rate of flow in a tube one-tenth the cross-sectional area of the converter. In technical design a linear flow rate of 10 metres per second is frequently taken as a convenient basis for calculation of gaseous reactions. Although fine division of the catalyst is desirable from the point of view of increasing the superficial area per unit volume of converter space, and although it may be possible to preserve uniform and approximately spherical packing in fine-grained material, yet, the increased skin friction caused by the great extension of surface to which the reactants are exposed during their passage, raises the value of the frictional loss or back pressure in the converter to such a high figure as to preclude economic working. A second objection of a practical nature to undue

eduction in catalyst size may be raised in that even coarse powders re very prone to removal by passage of the gaseous reactants, and are able to exhibit the phenomenon of "channel formation" due to light unevenness in the distribution of the material.

Types of apparatus for experimental work.—For the experimental investigation of catalytic processes involving gas reactions at a solid ontact substance, two simple types of apparatus may be described which have proved of great utility.

Sabatier developed a form of apparatus which has been used with success in the investigations which he has conducted with his ollaborators on the hydrogenation of organic liquids. This type of apparatus is generally applicable to the study of catalytic interaction of gases and of vapours of liquids.

A glass, or preferably quartz, tube of suitable dimensions forms the reaction space, in which is placed a layer of the catalytic agent to be employed —in the case of nickel a layer of the unreduced oxide.

One end of the tube is closed with a stopper carrying two tubes, as illustrated in the accompanying diagram (Fig. 6), of which one serves as delivery tube for the incoming gas (hydrogen in the case of hydrogenation studies), the other for delivery

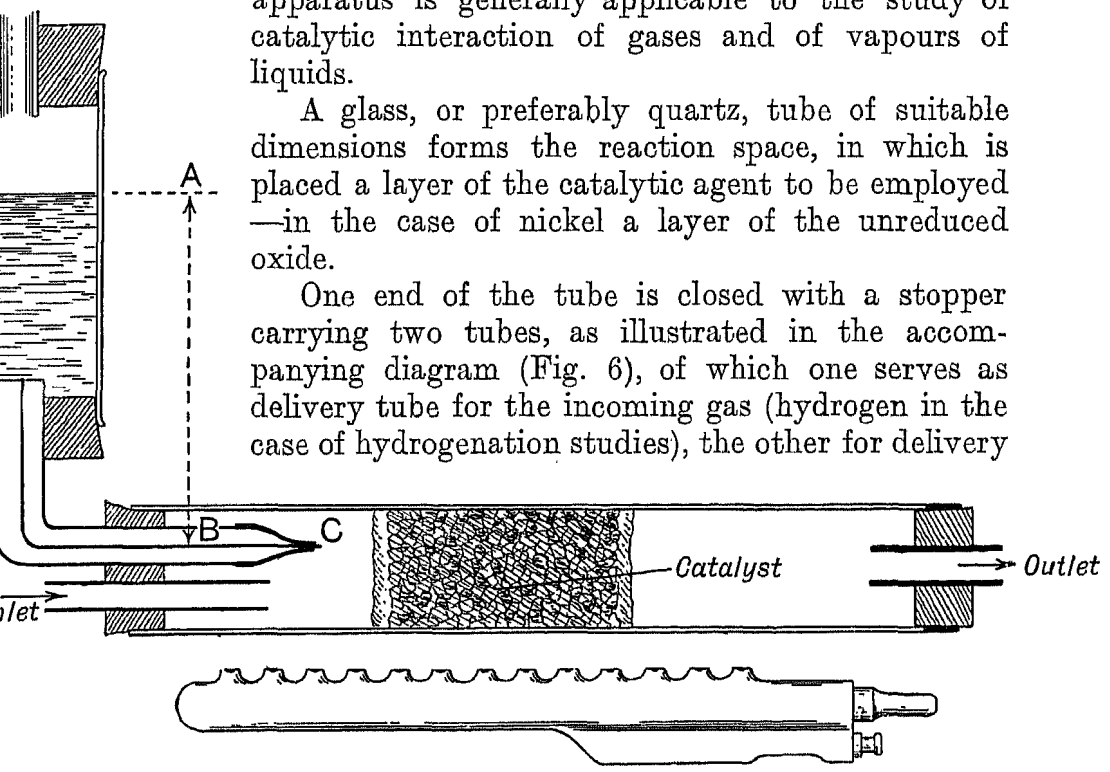


FIG. 6.

f the liquid, or of the gas to be investigated. In the case of liquids capillary tube is employed, the liquid being stored in the vertical ube T. The rate of flow of liquid may be regulated by varying the iameter of the capillary and the height of liquid in the reservoir. abatier recommends that the inflow of liquid into the reaction space e constant by arranging that it does not leave the capillary in drops. y allowing the end of the capillary C to touch the inside of the eaction tube this may be readily attained. If the reservoir T be onnected with a vessel of considerable dimensions the height of quid, AB, may be maintained reasonably constant over long periods.

The reaction tube is heated in any suitable manner, either by gas ame, as in an organic elementary analysis, or more conveniently for

the attainment of an even temperature, by means of an electr resistance furnace. In the latter case, where the heating is unifor around the tube, the catalyst may be inserted as a plug in the reacti space as alternative to the layer of material employed in the ga heated tube. The heating should extend sufficiently far along t tube to allow of vaporisation of the incoming liquid at C.[1]

With sufficiently volatile liquids, an alternative arrangement possible in which the mixture of the gas and vapour is obtained b allowing the former to bubble through the liquid, passing then direct into the reaction space. By regulation of the temperature of th liquid and by ensuring saturation of the gas at the given temperatur from a knowledge of the vapour pressures of the liquid, a definite rat of gas to vapour may be readily attained. The authors have foun this is a suitable method of introducing definite quantities of stea and alcohol vapours into the reaction mixture. It has been found however, advisable in the case of steam, first to supersaturate the ga with steam by passage through water maintained at a temperatur higher than that required to give the definite ratio, and then to pas the supersaturated gas through a further quantity of water maintaine at the requisite temperature.

Sabatier, in the case of solids which are readily vaporised, place the material in porcelain boats inside the reaction space some distanc before the catalyst mass. The incoming gas carries along with it th vapours of the solid arising from the heated boats.

The temperature employed may be determined according t Sabatier by means of a thermometer placed alongside the reactio tube, when the latter is embedded for evenness of temperature distri bution in a layer of heated magnesia or fine sand. Alternatively, i may be placed inside the reaction vessel, in which case, however, ther is difficulty in altering its position to determine the temperature a various points. With the latter alternative, a thermo-couple is mor useful than a mercury thermometer, owing to the difficulty of readin the latter when inside the tube.

A modified form of apparatus can be conveniently used, mor especially for the investigation of catalytic gas reactions at differen temperatures. The features of the apparatus are its simplicity and adaptability, ease of temperature control and observation, as well as evenness of temperature distribution. The accompanying diagram (Fig. 7) illustrates the salient details of the apparatus. The outside glass or silica tube is electrically heated by means of a resistance wire suitably insulated and lagged. The upper end of the tube terminates in a length of tubing of narrower bore sufficient to pass the thermometer or thermo-couple, which may be adjusted in position at any suitable

[1] Other modifications of this apparatus are described by Taylor and Neville, *J. Amer. Chem. Soc.*, 1921, **43**, 2060; Adkins, *ibid.*, 1922, **44**, 2177; Adkins and Nissen, *ibid.*, 1924, **46**, 139.

height. The catalytic material is contained in an inner concentric tube which, when in position, allows of a narrow space between the inside of the heater tube and the outside of the catalyst tube, through which the gases pass up from below and are thus brought to the desired temperature. By this arrangement, apart from the radiation across

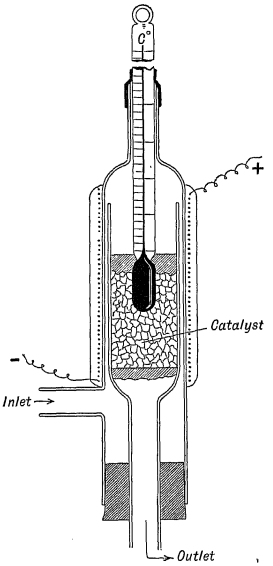


FIG. 7.

the gas space, the heating of the catalyst material is caused by the incoming gases, and so can be the more easily regulated. Also, the charging of the reaction space with the contact body is more readily effected than in the apparatus designed by Sabatier. Large sizes of this type of catalyst furnace, constructed in iron with suitable modifications, have been employed with considerable success in experiments upon a semi-technical scale.

CHAPTER V

PROMOTERS, MIXED, SUPPORTED, AND PROTECTED CATALYSTS

THE positive catalytic effect produced by a given substance in a given reaction may, it is found, be considerably enhanced by the admixture with the catalyst of small quantities of other substances. Normally, the acceleration produced by a catalyst is proportional to the concentration of the catalytic agent present, as will be illustrated in numerous examples in the following pages; in the case of two catalysts accelerating the same reaction, their double effect is frequently the same as if each were reacting singly. This is true, for example, when a mixture of colloidal platinum and gold takes part in the decomposition of hydrogen peroxide. But exceptions to this rule are common. Mercury and copper sulphates each accelerate the oxidation of aniline or naphthalene by concentrated sulphuric acid. Their joint effect is greater than the sum of their individual activities. More especially, however, in gas reactions accelerated by solid catalysts does the phenomenon referred to become pronounced. The modification of catalytic activity produced by even minute quantities of foreign materials is in many cases quite astonishing, and exploitation of this factor has been most marked in recent practical applications of catalysis. This may be illustrated by a textual quotation from the Badische Company's English patent[1] on improvements in the manufacture of hydrogen by the water-gas-steam catalytic process:

"In the researches on the production of hydrogen from mixtures of carbon monoxide and steam, according to the equation

$$CO + H_2O \rightleftarrows CO_2 + H_2$$

we have found that the power of catalytic agents generally can be improved by the presence of certain bodies which may be termed promoters. We have found, for instance, that the activity of the catalytic agents, especially those consisting of or containing iron, nickel or cobalt, or oxides thereof, and also the catalytic activity of other metals or oxides even such as, by themselves, are less active, can be greatly increased by the addition of certain compounds or

[1] No. 27963/1913.

bodies to which, as aforesaid, may be given the name promoters. Thus the activity of catalytic agents consisting of or containing iron, nickel or cobalt, or oxides thereof, can be greatly increased by the addition of oxygen compounds of chromium, thorium, uranium, beryllium, antimony, and the like. Further, a catalytic agent consisting of or containing iron in admixture with less than its weight of nickel, particularly after working for a long time, yields better results than does either iron or nickel when employed by itself. . . . In many cases, particularly when using catalysts of weak activity, we prefer to employ as promoter a compound which differs considerably from the catalytic agent, in particular with respect to valency, chemical basicity, and capability of reduction. . . . The contact masses containing iron as the catalyst agent, and a smaller quantity of nickel, as above described, as promoter, bring about rapid and far-reaching conversion without the simultaneous formation of methane, even when a comparatively low temperature is employed, and, as compared with pure nickel, are further characterised (especially when suitable oxides or oxy-compounds are employed as binding agents, or as promoters) by possessing greater stability and less sensitiveness to deleterious influences such as, for instance, fortuitous increase of temperature and impurities in the gas mixture."

As examples of such contact masses the patent application contains, *inter alia*, the following :

(1) The mixture obtained by evaporation and ignition of a solution of 85 parts of iron nitrate and 15 parts of chromium nitrate.

(2) The mixture obtained by ignition from a solution of the ingredients : 40 parts of ferric nitrate, 5 parts of nickel nitrate, and 5 parts of chromium nitrate.

(3) A preparation obtained by solution, evaporation and ignition of 194 parts of iron nitrate, 5 parts of ammonium bichromate, and 1 part of thorium nitrate.

Especially in this latter case is the principle of promoter action illustrated. It is clear from this example that a mixture containing, in the main, oxide of iron with admixture of but 2·5 per cent of chromium compounds and only 0·5 per cent of ceria, is claimed to have considerable superiority as catalyst over a contact mass containing iron oxide alone.

In addition to the use of promoted and mixed catalysts, consideration must also be given to the use of catalysts spread upon suitable supports. Stress has already been laid on the relation between physical condition and catalytic activity. Experiment has shown that efficient distribution of catalyst material may be secured by spreading the material upon an inactive support, economy of catalyst thereby resulting. The classical example is the use of finely divided platinum in the form of platinised asbestos or as platinised magnesium sulphate in the contact process of sulphuric acid manufacture. In

view of the phenomena occurring in the use of promoters and of mixed catalysts, it is possible that similar advantageous results accrue from the use of support materials, which are not to be explained from the point of view of distribution of catalyst alone. It is for this reason that the three classes of catalysts, promoted, supported, and mixed, are here grouped together for discussion.

Promoter Action

Information on the subject of promoter action is widely scattered through the literature and is in general meagre, being largely limited, in the field of heterogeneous catalysis, to simple statements in patent specifications that certain substances are able to activate some particular catalyst. Pease and Taylor [1] collected the major portion of this literature with the object of increasing interest in the investigation of this field. Their compilation has been followed by a number of communications, from various sources, dealing more especially with the mechanism of particular catalytic reactions. The results will be set forth in detail in subsequent paragraphs.

The definition of promoter action.—In attempting a definition of promoter action, Pease and Taylor construed the phenomenon very broadly and included *all those cases in which a mixture of two or more substances is capable of producing a greater catalytic effect than can be accounted for on the supposition that each substance in the mixture acts independently and in proportion to the amount present.* The breadth of this definition, while useful for purposes of literature compilation, has obvious defects. It is apparent that, within the scope of this definition, cases of promoter action, of mixed catalysts and of supported catalysts, may all be included. Furthermore, from what has preceded in reference to the relation of activity to distribution, it is apparent that the *amount* of a catalyst present is no correct measure of catalytic effect as witnessed by the extreme variability in catalytic activity per unit area of metallic foil and metallic mirrors noted by Hinshelwood, Hartley and Topley.[2] To define the field more particularly Pease and Taylor suggested the use of the terms "activation" and "co-activation", the former to designate the activation of a catalyst by a substance relatively inert catalytically, or by a small quantity of a relatively active substance. The co-activation of a number of catalysts each by the rest would obviously be a case which we have here designated as that of a mixed catalyst.

As far as a study of the literature has revealed, the term "promoter" was first applied in the patents of the Badische Anilin- und Soda Fabrik [3] on ammonia synthesis to the substances themselves inert [illegible] which are able to increase the activity of a moderately good catalyst

[1] *J. Physical Chem.*, 1920, **24**, 241. [2] *Proc. Roy. Soc.*, 1922, **100A**, 575.
[3] B.P. 19249, 16/8/10.

by admixture in small quantity with it. It can be maintained with some degree of success that the deliberate admixture of inert materials in small amounts with catalytic agents to improve the efficiency of the catalyst constituted a novel advance in the technique of contact catalysis. It is also certain, however, that this enhancement of activity had been achieved, unconsciously, many times previous to the deliberate use of such added agents. Indeed, as will later be shown, evidence as to the mechanism of the effect produced by such additions was obtained many years previously by Baxter in an investigation in no way connected with the problem of catalysis (see p. 107). The conscious development of this aspect of the subject by the Badische Company is well attested, however, by the patents covering a wide variety of catalytic processes in which the efficacious use of promoters was claimed. In addition to those already mentioned, the following may be cited. Thus, in hydrogenation processes, claim was made[1] for the use of iron, nickel, cobalt, or copper as catalysts, improved by addition of one or more of the following—often in quantities of less than 1 per cent: oxides or oxygen containing salts of the alkaline or rare-earth metals, or beryllium, manganese, magnesium, uranium, vanadium, nobium, tantalum, chromium, titanium, or boron, or difficultly soluble phosphates, tungstates, or selenates of the alkaline earths (or lithium), or compounds of fluorine, tellurium, or antimony, or the elementary tellurium or antimony. For the reduction of nitro-aromatic compounds, another patent[2] states that the copper used as catalyst may be considerably improved by the addition of zinc, silver, magnesium oxide, alumina, or sodium silicate. Other Badische patents[3] deal with the promotion of catalysts for use in the oxidation of ammonia. Iron oxide admixed with small amounts of bismuth oxide or with a mixture of bismuth and cerium oxides are examples of this class.

In their development of the field of promoted catalysts, with a view to patent protection, it is evident that the Badische Company attempted to extend the concept of a promoted catalyst to include cases which more particularly belong to the category of mixed catalysts. Thus, in ammonia synthesis, claims were made[4] for the use of mixtures of metals or their compounds from different groups or sub-groups of the periodic table. Another[5] claims the use of a catalyst which shall consist of one substance capable of absorbing hydrogen and another capable of absorbing nitrogen, palladium-molybdenum being cited as a catalyst. The inclusion of a 50-50 iron-molybdenum catalyst in a promoted catalyst patent clearly indicates the effort to include such cases of mixed catalysts in the general category of promoted patents. Such inclusions undoubtedly weaken any claim which the Badische Company might make to protection for promoted catalysts,

[1] D.R.P. 282782, 12/12/13; B.P. 2306, 28/1/14.
[2] B.P. 5692, 15/4/15.
[3] D.R.P. 283824, 14/4/14; 287009, 24/5/14; B.P. 13848, 18/6/14.
[4] B.P. 26167, 14/12/11.
[5] B.P. 21151, 25/9/11.

since there is an abundance of examples in the prior art of the superiority of mixed catalysts over either constituent singly. Thus in the case of ammonia synthesis itself, an Austrian patent granted to Hlavati [1] claims the use as catalyst of a mixture of titanium or titaniferous bodies in admixture with platinum. A French patent [2] to the Christiania Mine Kompanie claims titanium in a finely divided condition on neutral supports with or without the addition to the titanium of platinum or the platinum metals. Further, the titanium could be replaced by bismuth, antimony, or alkali or alkaline earth metals, provided that platinum or the platinum metals were employed. The use of metallic couples as reducing agents [3] is a very old example of the mixed metals possessing an activity when together much greater than the combined effect of each singly. In the case of the zinc-copper couple the reaction is not generally regarded as catalytic because the zinc reacts; but it is catalytic as regards the copper. Cohen and Dakin [4] report the catalytic action of an aluminium-mercury couple in the halogenation of benzene, toluene, and xylene. They state that the fragments of the couple remain unchanged during the reaction. These examples may be taken as typical. Other cases, more especially those of mixed catalysts in homogeneous systems, will be discussed at a later stage.

It would seem desirable, therefore, to restrict the term "promoter action" to the beneficial effect produced in a catalytic agent by admixture with a relatively small quantity of a material, inert or of negligible catalytic activity in the reaction in question. The higher activity obtained by using several catalysts mixed, over that obtained when they are employed separately, would then be a case of "co-activation". At the other extreme, the disposition of an active catalyst on a relatively large quantity of an inert or practically inert support material may be regarded as the production of a supported catalyst. It is very evident that the three classes will merge together, and no decisive line of demarcation between them can be drawn. It may be found also that the basis of the enhanced activity produced in all three types of product may, in certain cases, be the same. In other cases a marked differentiation of mechanism will be established.

Examples of promoter action.—Ipatiew appears to have been among the first to record in detail promoter action in a heterogeneous system. He found [5] that in the presence of copper oxide, and in a *copper* tube, amylene was only one-third converted into isopentane

[1] Austr. P. 45/2938, 1895. [2] F.P. 225183/1896.

[3] Gladstone and Tribe, *Proc. Roy. Soc.*, 1872, **20**, 218; *J. Chem. Soc.*, 1872, **25**, 461; 1873, **26**, 445, 453, 678, 961; 1874, **27**, 208, 406, 615; 1875, **28**, 508; 1876, **30**, 37; 1877, **31**, 561; 1878, **33**, 139, 306; 1879, **35**, 107, 172, 567; Williams, *Analyst*, 1881, **6**, 36; Ulsch, *Zeitsch. anal. Chem.*, 1891, **30**, 175; Thorpe and Eccles, *J. Chem. Soc.*, 1873, **26**, 541; Bothamley and Thompson, *J. Chem. Soc.*, 1888, **53**, 164; Muller and Wegelin, *Zeitsch. anal. Chem.*, 1911, **50**, 615; Harcourt, *J. Chem. Soc.*, 1862, **15**, 385; 1863, **16**, 289; Devarda, *Chem. Zeit.*, 1892, **16**, 1952.

[4] *J. Chem. Soc.*, 1899, **75**, 893; 1907, **79**, 1111. [5] *Ber.*, 1910, **43**, 3387.

by hydrogen at 200 atmos. at a temperature of 300° C. in twenty-eight hours; with copper oxide in an *iron* tube complete conversion was effected in twelve hours under the same conditions. The same relation holds also for the hydrogenation of tetrahydrobenzene, tetrahydrotoluene, pinene, and carvene.

Ipatiew also records [1] an interesting case in which a hydrogenation and dehydration catalyst appear each to activate the other when used together to carry out a reaction which ordinarily would involve several successive steps. He found that camphor was hydrogenated in presence of nickel oxide at 320°-350° C., yielding borneol. This in turn could be dehydrated by alumina at 350°-360° C., yielding camphene, which could then be easily hydrogenated at 240° C. to give camphene. By using a mixture of nickel oxide and alumina in presence of hydrogen the complete reaction could be effected at a temperature of 200° C. or less. Similarly, fenchone may be hydrogenated at 240° C. to give fenchenol, which, however, can only be dehydrated with difficulty. In presence of a mixed nickel oxide-alumina catalyst, a hydrogenation-dehydration process readily occurs at 215° C., yielding fenchane from the original fenchone.

The extraordinary increase in the light emissivity of thoria incandescent mantles when admixed with 0·9 per cent of ceria has been utilised, as is well known, in the technical development of the Welsbach incandescent mantle. A recent research [2] has established that a maximum in the efficiency of catalytic oxidation of electrolytic gas mixtures occurs at the same concentration of ceria in thoria. Upon this basis, it seems reasonable to assume that the mantle is a catalyst for the oxidation of illuminating gas, the ceria playing the rôle of promoter, more rapid combustion and a higher temperature of the mantle being thereby attained.

In the catalytic oxidation of ammonia, Maxted has obtained [3] curves indicating the relative efficiencies of iron alone and admixed with other metals as promoters. Bismuth, tungsten, and copper enhanced the yield of nitric acid with a given time of contact. Lead, manganese, and calcium diminished the yield. These observations are the basis of patent claims by Maxted and Ridsdale [4] for catalysts for ammonia oxidation.

The Harger-Terry patent [5] for the preferential catalytic combustion of carbon monoxide and oxygen in presence of hydrogen claimed, in addition to simple oxide catalysts, the use of promoted oxide catalysts. An iron catalyst containing 2·5 per cent chromium oxide and 0·5 per cent cerium oxide was found to be superior to an iron oxide catalyst, and operated more efficiently at considerably lower temperatures. The catalytic oxidation of carbon monoxide in air at room temperatures

[1] *Ber.*, 1910, **43**, 3387.
[2] Swan, *J. Chem. Soc.*, 1924, **125**, 780.
[3] *J. Soc. Chem. Ind.*, 1917, **36**, 777.
[4] B.P. 10781/1915; 126083/1916.
[5] B.P. 127609/1917.

can be achieved by mixed oxide catalysts,[1] of which the most notable is "Hopcalite", a mixture of 60 per cent manganese dioxide with 40 per cent copper oxide. This case is of especial interest since it has attracted considerable experimental study with a view to elucidation of the mechanism whereby the mixed catalyst is more efficient than either singly. This work is discussed in detail in the next section.

The mechanism of promoter action. — One case in which the mechanism of promoter action seems definitely to have been ascertained is available in the older literature. Elissafoff studied [2] the action of glass wool and heavy metal salts on the velocity of decomposition of hydrogen peroxide both singly and in conjunction with each other. Elissafoff showed that, together, the glass wool and heavy metal salt effected a much more rapid decomposition of the peroxide than would be anticipated on the basis of additive effects. Thus, with a decomposition velocity of 0·86 in presence of 0·5 grm. glass wool in 20 c.c. of peroxide, and one of 1·63 in presence of 1·54 millimolar solution of copper sulphate without glass wool, a solution with the same copper sulphate concentration plus 0·5 grm. glass wool in 20 c.c. gave a decomposition velocity of 10·8; all the velocity units are expressed in arbitrary units. The concentration of hydrogen peroxide was 12 millimolar. In this case at least the mechanism is apparent. It is known that the decomposition of peroxide takes place at the glass surfaces. It was probable that the copper salt was concentrated at the glass surface and so exercised greater effect. That this was so the following observations indicate clearly. The unimolecular constants for two copper ion concentrations of 1 and 10 millimols per litre were 0·0013 and 0·0023 respectively, in the ratio, therefore, of 1 : 1·77. The amounts of copper salt adsorbed from these solutions by Jena glass powder of the same glass were in the ratio of 1 : 1·73. It is apparent that the decomposition velocities are proportional to the amounts of adsorbed copper salt. This case is certainly, therefore, a reaction velocity at the surface and not a diffusion velocity. Were it possible to make adsorption measurements, other modes of decomposition of hydrogen peroxide would possibly be found to be of the same type.

Hydrogenation processes.—An informing contribution to the theory of promoter action has been made by Medsforth,[3] who has studied the effect of promoters added to a nickel catalyst in the hydrogenation of carbon monoxide and carbon dioxide to yield methane. Reasoning from the simultaneous production of water in the reaction, the addition of catalytic dehydrating agents to the nickel catalyst was made with material increase in the attainable reaction velocity for a given conversion of the reactants. Ceria, thoria, glucina, chromium oxide, alumina, and silica gave an, from seventeenfold to twelvefold, increase

[1] Lamb, Bray, and Frazer, *J. Ind. Eng. Chem.*, 1920, **12**, 217.
[2] *Zeitsch. Elektrochem.*, 1915, **21**, 352.
[3] *J. Chem. Soc.*, 1923, **123**, 1452.

in velocity over that obtainable with the straight nickel catalyst. Zirconia, molybdenum oxide, and vanadium oxide were somewhat less efficient, though still good, promoters. Tin and magnesium oxides, copper and silver metals, produced no acceleration over the straight nickel. With the carbon dioxide reaction the increases in velocity effected were somewhat less than those recorded for the monoxide reaction above. The order of efficiency was exactly the same. The order of efficiency is roughly that of oxide catalysts recorded by Sabatier in reference to strict dehydration processes.

In explanation of the activity of the promoters, Medsforth assumes the function of the nickel to be to assist the union of the gases to form a " complex " or intermediate compound of the methyl alcohol type, probably via formaldehyde. The promoter then functions as a catalytic dehydrating agent on the intermediate compound giving water and a methylene radical, whence, immediately, methane results. The promoter assists the known dehydrating action of the nickel. This can be schematised thus :

$$CO + 2H_2 \longrightarrow H_3C \cdot OH \longrightarrow \rangle CH_2 + H_2O.$$

The combined dehydrogenation and dehydration effected by Ipatiew[1] with a nickel alumina catalyst, whereby the conversion of camphor to isocamphene is effected at 200° C. in one step, is cited as supporting evidence.

Medsforth calls attention to an important feature of promoter action which he has noted, that of *selective promotion*. It would appear that when two reactions, both capable of being accelerated, take place at the same time in the presence of the same catalyst and the same promoter, that which is normally slower is accelerated to a greater comparative degree than that which is normally the faster. Support for this statement was obtained in the observation that when carbon monoxide and steam react in the presence of nickel and nickel promoters, whilst carbon dioxide and hydrogen are the main products, methane is also formed, the quantity of which is greater when, for example, alumina is present than when nickel alone is used. Similarly, in the production of methane from carbon monoxide and hydrogen, more carbon dioxide is formed as a by-product due to the simultaneously occurring water-gas reaction, when promoters are added to the nickel catalyst, than if this latter is used alone.

In discussing the applications of this dehydration hypothesis Medsforth reviews several cases of promoter action. For catalysis of the water-gas reaction with iron oxide as catalyst, it is significant that the promoters among the most effective are hydrating agents and oxygen carriers. The action of ceria-thoria in the incandescent mantle may also be in part due to combined oxygen carrier-dehydration effectiveness.

[1] *J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1695.

As a temporary classification of promoters for purposes of discussion Medsforth gives the following :

(1) The promoter decomposes intermediate compounds formed by the catalyst.

(2) The promoter causes the reacting substances to combine, the resulting intermediate compound being decomposed by the catalyst.

(3) The promoter adsorbs or combines with one of the reacting substances producing a greater concentration of the latter at the catalyst surface.

The origin of the carbon dioxide in the methanation process has been elucidated by Armstrong and Hilditch,[1] who have shown that when purified water gas is passed over nickel at 200°-300° C. the predominating reaction is $2CO + 2H_2 = CO_2 + CH_4$. The reaction is regarded as the sum of two reactions :

$$CO + H_2O = CO_2 + H_2,$$
$$CO_2 + 2H_2 + 2H_2 = CH_4 + 2H_2O,$$

the former of which is regarded as occurring in the same manner as the reaction in presence of copper previously studied by them,[2] namely, via formic acid, $CO + H_2O \longrightarrow HCOOH \longrightarrow H_2 + CO_2$. With cobalt the reaction commences at a lower temperature, 180° C., but the above reaction is subsidiary to the main methanation process, $CO + 3H_2 = CH_4 + H_2O$. Silver is inert, iron almost so, platinum and palladium of minor activity. Mixed catalysts were less efficient than the single catalyst. With nickel at increasing pressures up to 6 atmospheres the minimum temperature of interaction rises. The reaction yielding carbon dioxide and methane produces more methane from water gas than any of the other reactions. It may, therefore, have value as a means of increasing methane content or lowering carbon monoxide content of town's gas. The authors state that $CO_2 + H_2$ goes directly to methane and gives no carbon monoxide, so that partial reduction is apparently not taking place. This is at variance with some observations made in the laboratories of the Munitions Inventions Department in England, during the war, where methane prepared from carbon dioxide and hydrogen contained a small percentage of carbon monoxide.

In contrast to the conclusions of Medsforth cited above, Armstrong and Hilditch [3] conclude, with regard to the " promotion " of a straight hydrogenation process, the simple addition of hydrogen at an unsaturated linkage, in presence of nickel, alumina, silica, oxides of iron and magnesium being employed as promoters, that the stimulation observed can be satisfactorily explained on the basis of increased available catalytic surface of the nickel. There is some evidence of the removal or adsorption of catalyst poisons (sulphates in the precipitated oxides, or traces of impurities in the oil hydrogenated) ;

[1] *Proc. Roy. Soc.*, 1923, **103A**, 25. [2] *Proc. Roy. Soc.*, 1920, **97A**, 265.
[3] *Proc. Roy. Soc.*, 1923, **103A**, 586.

but these appear as minor influences compared to the effect on the extent of surface of nickel produced. They have been able to make an appreciably less amount of reduced nickel effect the same amount of action whatever the extent of the catalyst in alumina or other "promoting" oxide.

Armstrong and Hilditch [1] showed that the presence of sodium carbonate effectively promotes the hydrogenation of phenol at nickel surfaces. About 25 per cent by weight of nickel appears to give the maximum effect. In the presence of carbonate the reaction rate is more nearly linear than in the absence of the carbonate. This factor suggests that the function of the promoter is a protective one to the catalyst, keeping it free of inhibiting impurities.

Oxidation processes.—For the rôle of ceria in promoting the reaction between gases in ceria-thoria catalysed combustions, Swan concludes [2] that there are at least two possible explanations :

(1) The ceria behaves as an oxygen carrier during the combustion of the gases.

(2) The ceria, by increasing the electron emission of the thoria, causes a greater ionisation of the gases and more efficient combination.

This latter explanation could be experimentally tested.

Adsorption and the mechanism of promoter action.—In a research on the atomic weights of cobalt and nickel, Baxter investigated [3] the occlusion of hydrogen by the reduced metals and reached conclusions which are of fundamental importance in the study of catalytic action in general and promoter action in particular. Baxter found that the finely divided metals obtained by reduction of the oxides in hydrogen gas occluded relatively large amounts of the gas. He found that the volume of occluded hydrogen varies, in the case of the metal reduced from the oxide, with its purity and the temperature of reduction. The latter fact is of significance in the general problem of adsorption and catalysis, and, as such, has already been discussed in a preceding chapter. The former fact, the influence of impurities, has a marked bearing on the problem of the mechanism of promoter action. Baxter found that ordinary "chemically pure" oxide yielded a metal on reduction which occluded very considerably more hydrogen than oxide which may be designated of "atomic weight purity". Having traced the co-ordination between extent of surface and occluding power Baxter concludes that when impurities, for example, silica, are present in the oxide, the resulting metal is less compact than that obtained by identical treatment from the atomic weight purity oxide. In other words, a pure metal sinters more readily than a metal obtained by reduction of an oxide containing certain impurities. The fact that it is extent of surface which counts, cobalt ingots being known to occlude practically no hydrogen, makes it

[1] *Proc. Roy. Soc.*, 1922, **102A**, 21. [2] *J. Chem. Soc.*, 1924, **125**, 784.
[3] *Amer. Chem. J.*, 1899, **22**, 351.

certain that the phenomenon designated by Baxter as occlusion is, for the most part, what is now known as surface adsorption of the gas. A further fact of significance was Baxter's observation that the metal obtained by reduction of cobalt bromide occluded practically no hydrogen, and the presence of sodium bromide had no influence on the amount occluded. In other words, not all impurities present in the substance undergoing reduction are effective in promoting extension of metal surface.

Applied to the problem of the mechanism of promoter action, the experimental observations of Baxter obtained for quite different purposes may be summarised thus: (1) The presence of impurities in the materials from which catalytic metals are prepared may increase considerably the extent of adsorbing surface and, therefore, in agreement with earlier observations in a preceding chapter, may increase catalytic activity of the reduced metal; (2) certain impurities, for example, silica, are much more efficient than others, for example, sodium bromide, in producing extended surface. In these two observations we have two factors fundamental to the problem of promoter action, actual increase, by an added promoter, of the catalyst surface and specificity of promoting agent, the specificity being associated with the influence of the added agent on extent and nature of surface. Such studies must be multiplied by the student of catalysis with deliberate rather than accidental inclusions in the materials studied.

Two such cases have already been studied, one by Hurst and Rideal,[1] on adsorption of carbon monoxide and hydrogen, the other by Taylor and Russell.[2] In the latter work, measurements of adsorption by nickel obtained by reduction of the oxide, and of nickel-thoria from the oxide containing thoria as a promoter, have been made. Adsorptions of hydrogen and carbon dioxide were measured, since the researches of Medsforth already cited showed that the reactivity of these gases was much enhanced by the use of a nickel catalyst promoted by thoria. The experimental work shows that no proportionate increase in adsorption accompanies the activity shown by the promoted catalyst. The surface has therefore undergone a qualitative rather than a quantitative change. Whereas the promoted catalyst effects a tenfold increase in velocity over the non-promoted catalyst, the extension of surface, as measured by adsorption of either the carbon dioxide or the hydrogen at reaction temperature, only undergoes a 20 per cent increase. This is in harmony with the view of a composite catalyst surface with localised active centres. Even if it be assumed that the whole of the nickel surface capable of adsorbing hydrogen were catalytically active in the case of the promoted catalyst, it would follow that not more than 10-12 per cent of the surface of the unpromoted catalyst surface adsorbing hydrogen would have any catalytic

[1] *J. Chem. Soc.*, 1924, **125**, 694-705.
[2] *Dissertation*, Princeton, 1924; *J. Phys. Chem.*, 1925, **29**, 1325.

activity. Hurst and Rideal's results are discussed in the succeeding section.

One function of promoter action was suggested in the previous edition of this book (p. 31), in reference to the use of mixed catalysts for ammonia synthesis. It led to the conclusion that the original iron tended to adsorb or form a loose compound with a greater proportion of hydrogen to nitrogen than required by the stoichiometric ratio. The admixed catalysts, being in the main nitride-forming metals, for example molybdenum, would promote a more favourable hydrogen-nitrogen ratio. Bancroft extended this idea,[1] suggesting that the catalytic agent activates one constituent of the reaction chiefly and that the promoter activates the other. Some measure of activation will be necessary before such a conclusion can be experimentally tested. Experimental work on ammonia synthesis catalysts has not confirmed this point of view, thus simply outlined, but there is still no proved theory of mechanism in the ammonia synthesis reaction.

Interface phenomena and the mechanism of promoter action.— There are many places in the chemical literature which exemplify the statement that the molecules at the boundary between two phases are in a peculiarly labile or active state. Faraday observed that a perfect crystal of sodium carbonate or sodium sulphate refuses to effloresce until the surface is scratched or broken. He also observed that the efflorescence spreads from the injured place. Crystals of hydrated cadmium sulphate show this behaviour remarkably well. They are readily obtained in large and perfect form, which maintain a constant weight in a desiccated space until a boundary between a hydrated and a dehydrated phase is established. Langmuir[2] has shown that, in the dissociation of calcium carbonate by heat, the carbon dioxide is produced only at the boundary between the carbonate and oxide phases. The dissociation of silver oxide into its elementary constituents, studied by G. N. Lewis,[3] is a parallel case, Lewis observing that the rate of dissociation increased with increasing production of silver. Silver was termed the autocatalyst of the reaction. Reactions of this type occurring at an interface are necessarily characterised by an auto-accelerated reaction rate, since, initially, there is little or no interface at which reaction can occur, and, with increasing reaction, an ever increasing region of interface is produced. The different nature of the dissociation process when such interfaces are not set up is well illustrated in the case of mercuric oxide dissociation studied by Hulett and G. B. Taylor.[4] In this case, at temperatures where dissociation becomes marked, the mercury formed is also vaporised. No interface results and, so, no acceleration of the dissociation is obtained.

[1] *First Report, Committee on Contact Catalysis*, p. 16, 1922.
[2] *J. Amer. Chem. Soc.*, 1916, **38**, 2263.
[3] *Zeitsch. physikal. Chem.*, 1905, **52**, 310.
[4] *J. Physical Chem.*, 1913, **17**, 567.

As a result, passage of nitrogen gas for twenty-four hours over pure mercuric oxide at 500° C. gave concentrations of oxygen corresponding to only a few millimetres pressure, whereas the true equilibrium pressure at that temperature was upwards of one atmosphere. When interfaces were produced by the addition of foreign substances, iron oxide, manganese dioxide, and platinum, true equilibrium pressures were at once established, measurable both statically and dynamically. The researches of Kendall and Fuchs [1] on the accelerated decomposition of silver oxide, mercuric oxide, and barium peroxide in presence of other oxides is also illustrative of the effect produced by the deliberate creation of interfaces.

In a determination of the dissociation pressure of sodium bicarbonate, Lescœur observed [2] that the development of pressure occurs "slowly at first, then more quickly towards the end. It has seemed to me, moreover, that the final equilibrium was obtained more rapidly the more the proportion of dissociated salt increased." These observations are again characteristic of interface phenomena and are recognised in the technique of dissociation pressure measurements. A mixture of dissociating substance and product is normally introduced into the apparatus in which such measurements are made.

More recently, further evidence of interface phenomena in chemical decompositions is revealed by additional reaction velocity curves autocatalytic in nature. Sieverts and Theberath [3] studied the dissociation of silver permanganate and obtained such a reaction process. Small amounts of impurities increased the velocity of decomposition. Hinshelwood thereupon promptly called Sieverts's attention to his own work [4] upon both inorganic and organic compounds, some cases of which are interface phenomena.

Otto and Fry [5] thought that their results showed the decomposition of potassium chlorate to be a unimolecular process. Any one can see that they are in reality a beautiful example of an auto-accelerated process. Iron oxide promotes the decomposition. Recently [6] they have shown that potassium chloride does the same thing. The presumption is therefore strong that the process is an interface phenomenon. Neville has added [7] to this reaction an interesting case of promoter action. Impure pyrolusite was more effective than pure manganese dioxide. The pyrolusite contained 8 per cent iron oxide. A mixture of 8 per cent iron oxide and 92 per cent pure manganese dioxide had the same efficiency as the impure pyrolusite. The action of the mixture was more than additive of the effects of the two oxides separately; hence the promoter action, elucidation of the mechanism of which was not achieved. It will probably be quite complex.

[1] *J. Amer. Chem. Soc.*, 1921, **43**, 2017.
[2] *Ann. Chim. Phys.*, 1892, **25**, 430.
[3] *Zeitsch. physikal. Chem.*, 1922, **100**, 463.
[4] *Phil. Mag.*, 1920, **40**, 569; *Proc. Roy. Soc.*, 1921, **99A**, 203; *J. Chem. Soc.*, 1921, **118**, 721.
[5] *J. Amer. Chem. Soc.*, 1923, **45**, 1134.
[6] *J. Amer. Chem. Soc.*, 1924, **46**, 269.
[7] *J. Amer. Chem. Soc.*, 1923, **45**, 2330.

Proof that the enhanced reactivity at an interface was not confined to decomposition processes, but occurred in reactions between solids and gases, was forthcoming in a study by Pease and Taylor [1] of the reduction of copper oxide at moderately low temperatures by hydrogen. It was shown that low temperature reduction of copper oxide granules by hydrogen was negligible until copper nuclei had been established in the oxide mass. Subsequent reaction is then localised at the boundaries between the copper and copper oxide, as can be demonstrated visually by the ever increasing area of the red copper extending outwards from the original nuclei. The form of the curve of reaction rate is typical of an autocatalytic process. It evidently finds its explanation in the higher order of reactivity of an oxide ion adjacent to a neutral atom of copper over that of an oxide ion surrounded on all sides by a copper oxide lattice. Jones and Taylor [2] showed further that the low temperature reduction of copper oxide by carbon monoxide is also an interface phenomenon. Benton and Emmett have recently shown [3] that nickelous oxide reduction by hydrogen is of the interface type, while reduction of ferric oxide, which is known to form solid solutions with the lower oxides, shows a reduction curve which has none of the criteria of the interface type.

Langmuir [4] has pointed out that the hydration of a completely dehydrated substance should show the same auto-acceleration. There seems to be qualitative evidence of this in the dehydration of ethyl alcohol with " over-burnt " lime. In an experiment at room temperature it was found that, for two days, the lumps of lime remained intact in the alcohol. On the third day a small amount of powder appeared alongside the lumps of lime, while treatment for an additional twenty-four hours resulted in the complete disintegration of the lime lumps. Taylor noted [5] the reduction of copper oxide by both hydrogen and carbon monoxide was very pronouncedly retarded by the presence of oxygen in the reducing gas. This is most readily interpreted on the assumption that adsorbed oxygen protects the interface from attack by the reducing gas. The adsorption of oxygen by copper and by copper oxide is known to be small, so that it seems necessary to assume increased adsorptive capacity at an interface to account for the protective action observed.

In a study of the acceleration produced by the presence of oxygen in the union of hydrogen and sulphur, Norrish and Rideal [6] were led to formulate a mechanism for the accelerating action observed. The surface of the liquid sulphur was assumed to consist mainly of S_8 molecules, of which a few were opened and thus polarised. Adsorption of the gases was assumed to occur at the ends of the ruptured

[1] *J. Amer. Chem. Soc.*, 1921, **43**, 2179; see also Larson and Smith, *J. Amer. Chem. Soc.*, 1925, **47**, 346.
[2] *J. Physical Chem.*, 1923, **27**, 623.
[3] *J. Amer. Chem. Soc.*, 1924, **46**, 2728.
[4] *J. Amer. Chem. Soc.*, 1916, **38**, 2263.
[5] *J. Franklin Inst.*, 1922, **197**, 23.
[6] *J. Chem. Soc.*, 1923, **123**, 1689.

molecule. A strong attraction of the oxygen for the sulphur at one end of the chain, causing a weakening of the sulphur atom at the other end, would result in a more ready combination of such a sulphur atom with hydrogen.

Hurst and Rideal [1] applied the concept of interface activity to the problem of promoter action in processes of selective combustion. If a copper catalyst be promoted with small quantities of palladium and the ratio carbon monoxide to hydrogen determined for a series of such promoted catalysts, one of the following results may be anticipated. If the palladium causes no specific effect beyond a surface extension, the ratio CO/H_2 consumed will remain unaltered; alternatively, if promoting action is in reality an additive effect, then the CO/H_2 ratio will decrease with increasing palladium concentration, and the ratio should be capable of accurate calculation from both the known ratios of CO/H_2 for the copper and the palladium each in the pure state and from the stoichiometric composition of the catalyst. If, on the other hand, the addition of small quantities of palladium promotes the activity of the oxidised copper for carbon monoxide, we should anticipate a higher CO/H_2 ratio for small additions of palladium, rising to a maximum with subsequent increase in the palladium concentration, and finally falling to a CO/H_2 ratio higher than that for pure palladium at those concentrations where addition of copper promotes the palladium.

Hurst and Rideal found that small quantities of palladium, up to 1·70 per cent, increase the ratio of CO/H_2 burnt at any particular temperature in presence of a copper catalyst. A maximum occurs on the addition of 0·20 per cent. A promoted catalyst containing 1·70 per cent of palladium yields the same ratio as pure copper. Catalysts containing more than 1·70 per cent palladium yield a lower CO/H_2 ratio than copper, but higher than palladium. This increase in the ratio of CO/H_2 burnt on addition of small amounts of palladium is contrary to that which would be expected, as outlined in the preceding paragraph, either on the basis of extension of surface or the dilution of the catalyst surface with palladium. The result obtained is to be anticipated, however, if the reactivity of the oxidised copper at junctions such as Cu . Pd is affected.

To elucidate further the mechanism of the promoter action, Hurst and Rideal [2] studied the adsorption of hydrogen and carbon monoxide singly and in various mixtures on copper, palladium, and promoted catalysts. They conclude that the addition of palladium to copper produces an increase in the carbon monoxide adsorption and a decrease in the hydrogen adsorption, as well as a relative increase in the carbon monoxide of the adsorbed phase in the presence of both gases. The relative increase in the adsorption of carbon monoxide was found to be in good agreement with the relative increase in the ratio CO/H_2 consumed in the catalytic combustion process. The specificity of

[1] *J. Chem. Soc.*, 1924, **125**, 685. [2] *J. Chem. Soc.*, 1924, **125**, 694.

the effect on adsorption produced by the palladium promoter is further evidence that the promoter action is not merely due to surface extension but involves the further factor of the nature of the interface between catalyst and promoter.

Promoter action and concentration.—It may be anticipated that much useful information with regard to the mechanism of promoter action and to the nature of catalyst surfaces will result from a knowledge of the relationship between extent of promoter action and the concentration of promoter used. As yet, the quantitative evidence accumulated on this point is very meagre. Most of the statements concerning promoter action by added substances have no information which would indicate what the optimum concentration of promoter is for the given reaction.

The most comprehensive data on this point are contained in the contribution of Medsforth[1] already discussed. Medsforth studied the efficiency of promoter action in the synthesis of methane from carbon monoxide and hydrogen with nickel and nickel-promoted catalysts spread on pumice support, by ascertaining the maximum speed of gas passage over a given quantity of catalyst at which a given degree of conversion could be achieved. With nickel catalysts alone on pumice the desired conversion was achieved at a speed of 32-35 c.c. per minute. In the following table are recorded the speeds with which the same conversion is attained with various promoted nickel catalysts at various concentrations of promoter in the nickel catalyst.

Medsforth concludes that the tabulated results show no relationship between the molecular weight of a promoter and its optimum concentration. Some slight tendency, however, can be observed. With beryllium oxide the optimum concentration is around 20 per cent. With alumina this occurs at 15 per cent. Medsforth calls particular attention to the flatness of the curve of speed against promoter concentration once the optimum concentration has been passed. Thus, in the case of ceria, the range from 3 to 15 per cent promoter shows no variation in permissible speed of gas passage greater than the experimental error, although the promoter concentration varies five-fold. In discussing this feature, Medsforth distinguishes two cases, the one in which catalyst and promoter are deposited on a support, uniform distribution being assumed, the other in which the catalyst is deposited on the promoter.

As an example of the former, Medsforth discusses a nickel-thoria catalyst, with an optimum promoter concentration amounting to 10-12 per cent Ni by weight. From the relative weights of nickel and thoria, it is calculable that at the optimum concentration the surface of the promoter is approximately one-fortieth of the catalyst. An additional 1 per cent of thoria only increases the promoter surface

[1] *J. Chem. Soc.*, 1923, **123**.

an additional one-four-hundredth. With thoria present equal in weight to the weight of nickel the promoter surface is only one-fourth to one-fifth of the total. Hence, it may be concluded that around the

Promoter. Per cent of Ni.	Maximum Speed in c.c./min.						
	Ce_2O_3.	ThO_2.	GlO.	Al_2O_3.	Mo_2O_3.	V_2O_3.	Cu.
0·5	300	60	32	75	32	32	33
1	540	320	35	200	40	54	30
2	560	420	..	260	..	60	..
3	590	..	..	..	..	..	..
4	620	..	..	..	..	..	..
5	610	480	160	320	80	95	..
6	..	..	..	..	..	120	..
7	600	..	..	..	..	140	..
8	..	590	..	..	..	120	..
10	600	600	290	450	200	110	26
12	..	600	..	470	220	..	..
15	580	600	..	500	190	..	..
16	..	..	..	490	..	..	..
18	..	..	540	..	..	..	..
20	560	..	580	460	..	..	..
23	..	..	560	..	..	..	..
50	470	570	420	380	110	24	..
100	..	530	280	..	..	..	No action
200	380	470	..	..	..	..	..
About 400	..	350	..	..	..	..	..

optimum concentration marked changes in velocity with change in concentration of promoter would not be expected. Medsforth's data conform to this conclusion.

In the case of a catalyst deposited on a promoter the conditions are different. If it be assumed that 5 grms. of thoria can take up on its surface 0·1 grm. of nickel, the catalyst concentration is 2 per cent. A decrease in this concentration from 2 to 1·8 per cent means a change in surface of 10 per cent, so that when the catalyst is deposited at the surface of the promoter small changes in concentration of promoter produce important alterations in reaction velocity. Hurst and Rideal's [1] case of copper promoted by palladium is in this latter category. They found an optimum promoter effect at 0·2 per cent palladium. At a concentration of 1·7 per cent palladium, the catalytic activity had fallen to that of the unpromoted copper catalyst.

The surface conditions in promoted catalysts are obviously complex. A very considerable increase in the number of cases studied is much to be desired. Not only should the reactivity of the promoted catalyst be studied, but determinations of adsorptions on the same samples as are used for the activity tests should also be made. The adsorptions

[1] *J. Chem. Soc.*, 1924, **125**, 685.

should reveal more readily the changes in the surface conditions. Simplification of the problem would be secured by eliminating all support materials in such experiments, since they introduce a new variable into an already complex problem. Hurst and Rideal made one set of adsorption measurements on their promoted copper catalyst, which showed the variation in adsorption previously recorded. It is to be regretted that similar measurements on the whole series of promoted catalysts were not made. If the adsorption measurements were coupled with measurements of heat of adsorption, some data on the problem of activation by promoters might also be secured.

The really interesting problem which the study of promoter action in its relation to concentration suggests is the reason why such minute amounts of promoter effect such marked changes in activity. Thus, in the case studied by Medsforth a concentration of 0·5 per cent ceria in the nickel catalyst causes a tenfold increase in reaction rate. Assuming uniform distribution of promoter in the catalyst, this represents one molecule of ceria in every 1130 atoms of copper in the catalyst surface. This minute change in surface concentration brings about a tenfold increase in catalytic activity. This strongly suggests that, of the atoms in the surface of a catalyst, very few indeed possess marked catalytic activity. Armstrong and Hilditch,[1] discussing the small amount of toxic material necessary for total suppression of catalytic activity, conclude that it is probable that an active catalyst is merely an average term expressing a surface on which a number of patches of maximum activity occur, the greater part of the surface being of perhaps a quite low order of activity. This opinion, based upon a study of poisons, is at one with the view put forward here with respect to the mechanism of promoter effect in minute concentrations. In Chapter VI., in the discussion of poisons, the quantitative evidence for this point of view will be detailed.[2]

The mechanism of co-activation. — Conclusions parallel to those just recorded as to the mechanism of promotion in hydrogenation processes have been reached by several workers in respect to the mechanism of co-activation found in the use of mixed oxide catalysts in oxidation processes. Extent of adsorption, the nature of the adsorbed gases, enhanced activity at interfaces, the removal of impurities by the added agent, and the influence of the admixed substance on the rates of several component reactions of the process are all cited in the succeeding paragraphs.

Bray and Almquist[3] attribute the activity of a mixture of two oxides to an increase in the rate of desorption of reaction products,

[1] *Trans. Farad. Soc.*, 1922, **17**, 670.

[2] For a detailed discussion of the concept of a composite catalytic surface with isolated centres of high activity see Rideal, *Conseil Solvay*, April 1925. Taylor, Report, *Committee on Contact Catalysis, J. Phys. Chem.*, 1926. Also Pease, *J. Amer. Chem. Soc.*, 1928, **50**, 1037, 1054.

[3] *J. Amer. Chem. Soc.*, 1923, **45**, 2305.

or an increase in the rate of reaction within the film, due to what ma be considered a partial chemical reaction between the two oxides, neutralisation of the valence forces of each other.

Whitsell and Frazer [1] conclude that manganese dioxide is the initia cause of oxidation at low temperatures in Hopcalite mixtures. Th oxidation process may be catalytic or occur at the expense of the oxid oxygen. The purer the catalyst, that is, the freer from adsorbed potash the more rapidly was it able to take up oxygen fast enough to mak the process catalytic. This points to a mechanism of alternate oxida tion and reduction. Too strong ignition of the preparations, eve though alkali-free, gave a dense product resembling natural manganes dioxide and entirely inactive. Whitsell and Frazer also incline to th view that the cupric oxide in a mixture may cut down adsorbed alka or affects the way it is held, so that its poisonous effect is annulled They note that pure manganese dioxide and mixtures of this wit copper oxide lose oxygen to the air at room temperatures, and tha the activity because of this is greatly increased by the fineness o division of the particles.

Benton [2] attacked the problem of co-activation by studying ad sorptions of carbon monoxide (and hydrogen) by various oxides an mixtures. He concludes that there are two types of adsorption, primary, specific adsorption, chemical in nature, and a secondary physical, or pore adsorption. By comparison of the adsorptions o oxygen, carbon monoxide, and carbon dioxide he deduces the relativ magnitudes of primary adsorption of the monoxide on various oxide and mixtures, and shows that the order of such adsorption is the orde of their catalytic activity in oxidation processes. He concludes therefore, that primary adsorption of carbon monoxide is the firs stage in the catalytic process, and is followed by desorption of carbo dioxide. Benton shows that there is no parallelism between secondar adsorptions and catalytic activity, and that, therefore, if total ad sorptions measured include both primary and secondary adsorptions such total adsorption may give no clue at all with respect to catalyti activity. He concludes that, on silica and charcoal, adsorptions ar largely physical or secondary, with conspicuous exceptions in the cas of charcoal with the gases oxygen and chlorine.

Promoter Action and Co-activation in Homogeneous Catalytic Reactions

The outstanding example of promoter action in homogeneou systems is the well-known neutral salt effect in reactions catalysed by the hydrogen ions of strong acids. The inversion of cane sugar, th hydrolysis of esters, the dehydration of hydroxy acids to form lactones keto-enol tautomerism, and other reactions catalytically accelerate

[1] *J. Amer. Chem. Soc.*, 1923, **45**, 2848. [2] *J. Amer. Chem. Soc.*, 1923, **45**, 887, 900.

by the use of strong acids, all provide this interesting case of promoted catalysis. If, in addition to a strong acid, a neutral salt of that acid is added to the reaction mixture, it is found that the velocity of reaction is increased. As the neutral salt alone has no appreciable catalytic effect, the case is one of simple activation or promoter action rather than of co-activation. It is beyond the scope of this section to detail all the work which has been accomplished or the varied views which have been put forward to explain this phenomenon. They will be separately treated in subsequent sections of the book. It is desirable, however, to point out here that the many attempts which have been made to account for the phenomena all have this in common, that they attempt to account for the observed acceleration by assumptions, for which experimental evidence is also sought, as to the concentration of either the catalyst on the reacting species or both. And the belief is common to all the investigators concerned that, when these several factors shall have been successfully stated, the observed acceleration will be found to be consonant with the ordinary laws of reaction kinetics. This attitude of mind might well be adopted by workers in all branches of the study, not only of promoter action but also of catalysis generally.

Price [1] studied very thoroughly the interaction of potassium persulphate and potassium iodide,

$$K_2S_2O_8 + 2KI = 2K_2SO_4 + I_2,$$

and the influence of catalysts on the same. He found that ferrous sulphate was a good catalyst, copper sulphate less efficient. Both these catalysts accelerated reaction in proportion to their concentrations in the reaction mixture, but the effect of the two salts together was more than additive. The accelerations observed always exceeded those calculated on the assumption that the individual activities were additive. Manganese and zinc sulphates, which are themselves only slightly active, gave additive results when mixed with copper sulphate. With ferrous sulphate, on the contrary, the observed acceleration was less than the calculated result. Price was unable to give a reason for the catalysis observed or for the co-activation.

The oxidation of hydriodic acid by hydrogen peroxide in presence of iron and copper salts was studied quantitatively by Brode.[2] He showed that ferrous sulphate was a very good catalyst, copper sulphate a poor accelerant. When together, however, one mol of copper sulphate in 100,000 litres was readily manifest. This joint action of the two salts had previously been employed by Traube [3] in testing for hydrogen peroxide in the presence of acids by means of starch-potassium iodide. The iron-copper salt mixture is active in concentrated acid solutions, whereas in such solutions iron salts alone are inactive. Neither iron

[1] *Zeitsch. physikal. Chem.*, 1893, **27**, 474. [2] *Zeitsch. physikal. Chem.*, 1901, **37**, 257.
[3] *Ber.*, 1884, **17**, 1062.

nor copper sulphates increased the catalytic activity of molybdic c tungstic acid when used as an additional catalyst in the reaction Molybdic and tungstic acids also behaved additively when used together

Bohnson and Robertson [1] have made a very thorough study c the mechanism of this activation of iron salts by copper salts in th decomposition of acid solutions of hydrogen peroxide. They fin that for a given concentration of iron salt, either sulphate or chloride there is a maximum rate of reaction with about one millimol of adde copper salt per litre. This maximum effective concentration of coppe appears to be independent of the concentration of iron salt. Th extent of promotion (measured by the promotion factor which is th ratio of the maximum rate to the normal rate for iron alone) is in dependent of the acid concentration and temperature. The exten of promotion is much greater for ferric sulphate than for ferric chloride although the maximum rate obtained in each case is the same. Th promotion factors for the two systems approach each other as th concentration of iron approaches zero.

As to the mechanism of the promoter action Bohnson and Robertson conclude that the facts are best explained thus: (*a*) the iron salt is the primary catalyst by virtue of its ability to form an intermediate compound, probably H_2FeO_4; (*b*) the copper salt is a secondary catalyst accelerating both the formation and subsequent decomposition of the intermediate product. The effect of the secondary catalyst is dependent upon its concentration only for very small quantities, a maximum effective concentration being noted. The mechanism of the secondary catalysis has not been explained. That the suggested secondary action is real is deduced from the following experiment. Two equal portions of a solution of barium ferrate in acetic acid were allowed to react with equal quantities of hydrogen peroxide. To one of the samples a very little copper acetate was added. The oxygen was evolved much more rapidly in this than in the one to which no copper salt was added. It may be observed that the effect is peculiar to copper compounds, since nickel, cadmium, mercury, barium, lead, cobalt, zinc, tin, and magnesium salts appear to retard the reaction in presence of iron salts. In sulphate systems, silver appears to have a slight accelerating effect. This singular behaviour of copper is probably significant in the solution of the problem of the secondary catalysis.

Bredig and Brown [2] have found that in the catalytic oxidation of aniline by sulphuric acid, according to the equation

$$(C_6H_5NH_2)_2SO_4 + 28H_2SO_4 \longrightarrow (NH_4)_2SO_4 + 28SO_2 + 12CO_2 + 3H_2O,$$

copper sulphate and mercurous sulphates are together more active than their separate catalytic activities would suggest. Bredig and

[1] *J. Amer. Chem. Soc.*, 1923, **45**, 2512. [2] *Zeitsch. physikal. Chem.*, 1903, **46**, 502.

Brown consider that a reciprocal oxidation and reduction of copper and mercury may be the cause of the unusual results. Only one series of data is given in the research. Hence, it is not possible to say whether either one of the two is particularly susceptible to activation or what relation holds between the acceleration noted and the proportion of salts present. Further work is needed to elucidate these points. The mechanism suggested by the above equation seems also to be impossibly complex, although Bredig and Brown say that the equation quantitatively represents the course of events in very dilute aniline solutions.

Supported Catalysts

The form of the catalyst. — In contact catalysis, the form of the catalytic agent is of considerable importance. The striking feature common to most of the contact catalysts is their porous or finely divided structure. Indeed, this structure may be regarded as characterising the successful contact agent. In several cases the preliminary phase of activation of a catalyst is accompanied by a change from a massive form to a finely divided structure. Thus, the platinum gauze catalysts used in the oxidation of ammonia by air or oxygen at high temperatures change from a smooth, plane-surfaced wire to a corrugated material. Similar changes in physical form are shown by silver gauze [1] when used for the catalysis of hydrogen-oxygen mixtures. The catalytic activity of copper wire can be greatly enhanced by submitting it to alternate oxidation and reduction of the oxide at successively lower temperatures. In this way copper catalysts can be secured which will promote oxidation of carbon monoxide, admixed with air or oxygen, at a temperature of 100° C. The copper wire suffers, in the process, a physical change similar to that with platinum and silver. These several methods of activation are, in reality, the production of supported catalysts. The wire core acts as a support material for the active, finely divided material produced on the surface by the process of activation. The mechanism of the activation [2] is to be ascribed partially to the increase in surface area of catalyst; that is, the adsorption per unit mass of catalyst is increased with a resultant increase in reaction per unit mass in unit time. The activation, however, also results undoubtedly in a change of the nature of the adsorption per unit surface of area. The evidence previously cited, and confirmed in a later section in the discussion of poisons, that a catalyst surface is in reality a surface on which a number of patches of maximum activity occur, the greater part of the surface being of low activity, when applied to this problem of activation of massive wire catalysts indicates that in the activation process the number of positions of maximum activity is markedly

[1] Bone and Wheeler.

[2] Bancroft, *First Report, Committee on Contact Catalysis*, 1922; Langmuir, *Trans. Farad. Soc.*, 1922, **17**, 607; Taylor, *J. Franklin Inst.*, 1922, **197**, 1.

increased. The disordered arrangement of metallic atoms produced in the activation process is more favourable to the existence of such active patches than is the normal crystal-lattice arrangement of the atoms in a smooth-stranded wire. Langmuir believes that the activation process may also operate favourably to catalysis by changing the normal spacing of the atoms to one more favourable for the adsorption of the reacting gas molecules in such configurations as are conducive to interaction. These several points of view with respect to the mechanism of activation have only received the beginnings of experimental verification. Full experimental confirmation is to be desired.

In the production of active catalytic agents the method of conduct of the process frequently yields a supported catalyst without general recognition of the fact. Kelber showed[1] that nickel oxide *per se*, when reduced at about 300° C., gave a moderately active catalyst, but when reduced at 450° C. gave a product of but feeble activity. Nickel oxide deposited upon kieselguhr and reduced at 450° C. gave a catalyst much more active than the metal catalyst prepared at 300° C. These conclusions were confirmed by Armstrong and Hilditch,[2] who showed that a reduction at higher temperatures gives rise to considerable shrinkage in the volume of the metal catalyst. This shrinkage and loss of catalytic activity is largely suppressed if the active material is spread upon an inert support. These facts are apparent from the data of the following table.

Nickel Oxide.				Reduced Nickel.		
Source of Material.	Density.	Apparent Volume in c.c.	Reduced at	Density.	Apparent Volume in c.c.	Catalytic Activity.
Powdered fused oxide .	6·96	0·35	500° C.	8·14	0·52	None
Precipitated hydroxide .	5·41	0·87	300° C.	7·85	0·83	Fair
Do. .	5·41	0·87	500° C.	8·18	0·56	Very little
Oxide on kieselguhr .	1·63	3·22	500° C.	1·85	2·67	Very active

In discussing these results, Armstrong and Hilditch remark that "it has frequently been observed, with unsupported nickel oxide, that partially reduced oxide is more active than the same when completely reduced. Since, as our bulk gravity figures show, there is a tendency to contraction when a light, precipitated oxide is reduced, it is obvious that a partially reduced oxide will consist of a film of nickel dispersed over the central core of each particle, and it is practically certain that the superior activity of this product over the fully reduced

[1] *Ber.*, 1916, **49**, 55, 1868. [2] *Proc. Roy. Soc.*, 1921, **96A**, 490.

metal is due to its being a 'supported' catalyst (nickel distributed on nickel oxide) and therefore of the same type, although not of the same degree of activity, as nickel upon a support such as kieselguhr."

The superiority of the catalyst spread upon kieselguhr is to be attributed to the nature and extent of distribution of the metal and to the fact that the support does not shrink upon heating, its bulk determining, almost wholly, the bulk of the final product. The support acts as an anchor to the metal deposited upon it and inhibits the sintering or crystallisation which occurs with the unsupported catalyst. The occurrence of sintering with the unsupported catalyst is readily seen from the data in the previous table at 300° C. and 500° C. for the reduction of the hydroxide, the apparent volumes at the two temperatures being 0·83 and 0·56 respectively. This sintering occurs with most unsupported catalysts not only at high reduction temperatures but also when catalysts prepared by reduction at low temperatures are subjected to successively higher temperatures. The sintering is roughly characterised by the change in apparent volume. The change of adsorptive capacity of the sample is, however, a much more sensitive criterion of the occurrence of sintering.[1] The extent to which this occurs may be illustrated by the following figures [2] on unsupported copper and nickel before and after a heat treatment following a reduction:

Catalyst.	Heat Treatment.	Adsorption of Hydrogen at 0° C. and 760 mm.
A. 100 gm. active Cu	No heat beyond reduction of oxide at 200° C.	3·70 c.c.
B. ..	A. Heated to 450° C. for 1·5 hours	1·15 „
C. 27 gm. active Ni	Obtained by reduction of oxide at 300° C.	35 „
D. ..	C. Heated at 400° C. for 4 hours	16 „

Adsorptive capacity is also a good index of the extent of distribution of the metal catalyst on a suitable support material, and also of the non-sensitivity of such a supported catalyst to heat treatment. Gauger and Taylor [3] readily obtained adsorptions amounting to 5 c.c. per gram of nickel at 0° C. and 760 mm. with this catalyst spread on diatomite brick. The most highly adsorptive sample of unsupported nickel prepared in the same manner showed an adsorption of 1·3 c.c. hydrogen per gram of nickel under the same circumstances. There is reason to believe that this sample was in reality a supported catalyst, namely, a partially reduced sample, nickel on a nickel oxide support. Furthermore, in contrast to the data on unsupported nickel catalysts cited in the previous table, nickel catalysts on diatomite

[1] Taylor, 3rd Report on Cont. Cat., *J. Phys. Chem.*, 1924.

[2] Pease, *J. Amer. Chem. Soc.*, 1923, **45**, 1196, 2235; Beebe and Taylor, *J. Amer. Chem. Soc.*, 1924, **43**, 43.

[3] *J. Amer. Chem. Soc.*, 1923, **45**, 920.

brick could be prepared by reduction at 500° C., or could be subjected to heat treatment at such temperatures, without loss of adsorptive capacity. Pollard [1] found that adsorption measurements could not be duplicated satisfactorily with platinum black, as the gases could not be pumped off completely without heating to 300° C., at which temperature the platinum sinters to such an extent that the adsorption changes very much. Platinised asbestos, however, can be heated to 400° C. without undergoing any change.

The increased catalytic activity per unit mass of catalytic agent employed, secured by spreading the catalyst on a support, means economy of material in the catalytic operation. It is for this purpose that the more expensive contact agents were thus first supported, the use of platinised asbestos and platinised magnesium sulphate being good examples. At the same time, other desirable properties in the catalyst may be secured. If a catalyst material be too fine, considerable resistance is offered to the passage of reacting gases, and this frequently results in channelling through the contact mass, with a corresponding decrease in efficiency. The incorporation of the catalytic mass upon a suitable support may obviate such difficulties. In exothermic catalytic reactions there is the danger that overheating, and consequent destruction of the activity, of a catalyst mass may occur. Quite recently in such cases use has been made of the metal aluminium as catalyst support material, thermal equilibrium in the catalyst system being thereby facilitated.[2] The metal support is employed in a granular form, obtained by allowing the molten metal to cool slowly in trays, the mass meanwhile being vigorously shaken.

Support materials and poisons. — Rosenmund and Langer [3] have shown that the nature of the support material is of importance in protecting the catalyst against poisons as well as in influencing the catalytic activity. With palladium catalysts on various supports the influence of arsenious oxide and carbon monoxide as poisons was studied, in the reduction of cinnamic acid. Kieselguhr-palladium catalysts showed the least activity and greatest sensitivity to poisons. Blood charcoal gave the most active and most resistant preparations. In these two cases activity and resistance run parallel. Barium sulphate supports are more active than pumice; the latter are more active in presence of the poisons. The effect of the supports is evidently a function of the adsorptive capacity of the support for the poison. It acts in these cases as a purification agent in the catalyst system.

Adsorption of reactants by support materials. — It is possible that one of the functions of the support material is to provide the catalyst with a reservoir of one or more of the reactants. Thus, R. A. Beebe [4]

[1] *J. Phys. Chem.*, 1923, **27**, 356.
[2] Barrett Co., Edgewater, N.J.; Stockholm's Superfosfat Aktiebolaget, S.P., 1921.
[3] *Ber.*, 1923, **56**, 2262.
[4] Thesis, Princeton University, 1924; *J. Phys. Chem.*, 1925, **29**, 1325.

has shown that asbestos, suitable for use as a support for platinum in the production of contact mass for sulphur dioxide oxidation, adsorbs 0·79, 0·10, and 0·04 c.c. of nitrogen and 53·0, 11·3, and 2·0 c.c. of sulphur dioxide per gram at 0°, 110°, and 218° C. respectively. Similarly, magnesium sulphate was shown to adsorb marked quantities of the same gases. Diatomite brick, which forms a good support material for the cuprous chloride used in the oxidation of hydrogen chloride by the Deacon chlorine process, can be shown to adsorb large amounts of hydrogen chloride. Russell [1] has shown that pumice used as a support for nickel adsorbs 1·2 c.c. of nitrogen per gram at 110° C., and still larger quantities of carbon dioxide. The question as to whether this adsorption by the support of one of the reactant gases facilitates the progress of the catalytic reaction has still to be decided. More must be learned concerning the mechanism and characterisation of activation of reacting species. In the meantime the existence of such adsorptive capacities by the support materials must be remembered when measurements of adsorption by contact materials spread upon supports are being made.

Nature of support materials.—A variety of substances have been employed as support materials. In addition to those already alluded to, mention may be made of glass, wool and silica fibres, fibrox, various porous siliceous materials such as fireclay, alundum, and unglazed porcelain, the various forms of charcoal, anhydrous salts and porous oxides obtained by calcination of suitable materials or by dehydration of gelations, precipitates or gels.

Gels as support materials.—Considerable attention has been devoted recently to the use of gels as support materials for catalytic agents, and some striking results have been indicated. An impetus was given to this work by the development of the technical production of silica gel adsorbents by Patrick [2] and of base-exchanging silica gel and alumina-gels by Wheaton and J. Crosfields.[3] Patrick has patented [4] the use of impregnated silica gels as catalytic agents, having mentioned specifically the production of platinised silica gels for sulphur dioxide oxidation. He has shown also that silica gels impregnated with iron oxide show marked efficiency in the oxidation of sulphur dioxide. As an example of the preparation of such a gel, Patrick cites the production of an iron oxide gel. One hundred c.c. of a 5 per cent ferric chloride solution is mixed with 200 c.c. of sodium silicate containing 1 per cent Na_2O. After the mixture has set, the gel may be broken up and washed free from chlorides without loss of iron. The impregnated ferric oxide may be reduced to iron by the action of hydrogen. In place of the silicate, an aluminate, stannate, titanate, tungstate, or zirconate may be used. The products cited in the patent include silica with iron, copper, or

[1] Thesis, Princeton University, 1924; *J. Phys. Chem.*, 1925, **29**, 1325.
[2] B.P. 136543/1919; U.S.P. 1297724/1919.
[3] B.P. 177746/1922.
[4] B.P. 159508/1921.

nickel, silica and iron oxide with copper, magnesium, cadmium, zinc, and manganese oxides, and silica and alumina with copper oxide.

Reyerson and Patrick [1] have studied metal-impregnated silica gels obtained by reducing metals from solutions of their salts by means of hydrogen adsorbed in silica gel at $-20°$ C. The metals form a black deposit on the gel, and in the case of palladium, platinum, and copper marked reaction between hydrogen and ethylene has been obtained at room temperatures.

Choice of support materials.—The choice of material to be employed is generally determined by processes of experimentation. As with the choice of catalysts generally, no sure guiding principles can be laid down. Experience shows, however, that in a great many cases use of a given catalyst support brings about a serious diminution in catalytic efficiency, generally attributed to a functioning of the support as a negative catalyst. Obviously, with a catalyst which is poisoned, for example, with sulphur, the presence of sulphur in the catalyst support is not permissible. The extraordinary sensitivity of certain catalysts to minute impurities restricts severely the number of possible supports. In reactions which are conducted at high temperatures, also, the possibility of interaction between catalyst and support material must be constantly envisaged. Especially in the case of oxide catalysts is this necessary, owing to the ease of combination with siliceous materials with formation of non-active silicates. In such cases, catalyst supports which are basic in character are to be favoured. The ideal support, therefore, should be a porous material, free from impurities negatively catalytic to the contact body, incapable of interaction with the catalyst, and, if possible, itself positively catalytic, even though feebly so, to the reaction in which it is to be employed.

Protected Catalysts

Colloidal catalysts when employed in catalytic reactions oftentimes lose their activity by agglomeration of the colloidal particles. The decrement in surface thereby resulting is reflected in a decrease in catalytic activity. Such colloidal catalysts may be stabilised by the addition of various agents, and the use of such "protected" colloidal catalysts is now standard practice. Paal and his co-workers [2] made use of a water-soluble protective colloid, the sodium salts of protalbinic or lysalbinic acids, to stabilise colloidal platinum and palladium. Skita,[3] who has detailed in a comprehensive manner the literature of the subject, employed an acid stable protective colloid such as gum arabic. Gelatine and glue have also been employed.

[1] *Colloid Symposium Monograph*, p. 119; Madison, Wis., 1923.

[2] *Ber.*, 1905, **38**, 1398, 1406, 2414; 1907, **40**, 1392, 2201, 2209; 1908, **41**, 805, 2273, 2282; 1909, **42**, 1544, 1553, 2239, 3930; 1913, **46**, 1297.

[3] *Ber.*, 1911, **44**, 2862; 1912, **45**, 1627.

The function of the added agent is to protect the colloid particles from agglomeration in the reaction media in which they are placed. This is brought about by the presence of the protecting agent on the outside of the particles of colloidal catalyst. The stabilisation thereby secured is obtained, however, at the expense of the catalytic activity. This was shown by Gröh [1] in the stabilisation of colloidal platinum by gelatine. Even small quantities of the gelatine exert a most marked retarding influence on the rate at which hydrogen peroxide is decomposed by the platinum, as the following table shows:

Per cent Gelatine.	Time for Half Decomposition.	Per cent Gelatine.	Time for Half Decomposition.
0·000	100	0·05	620
0·001	437	0·10	983
0·01	460	..	..

The gelatine, however, increases the stability of the colloidal metal solution, and tends to prolong its period of activity by preventing its precipitation by electrolytes.

Rideal [2] studied the protective action of gum arabic on colloidal platinum or palladium in the catalytic hydrogenation of phenyl propiolic acid. It was found that gum arabic in small amounts increased and then in larger amounts decreased the rate of the reduction process when the sols were prepared in the presence of the protective agent. The increase is to be attributed to an increased dispersion of the colloidal metal brought about by the presence of the protecting agent. In studying mixed platinum and palladium sols, Rideal found that "in all cases where the sol was prepared from platinum containing small quantities of palladium there was a very marked improvement in stability and resistance to age over those prepared from the pure salts. This suggests the hypothesis that promoters may function in part as peptising agents for colloidal catalysts or for catalysts which pass through a colloidal stage at some point in their preparation." Bancroft points out [3] that in addition to the possibility of increased dispersion, it is also possible that the reaction may take place more rapidly at the interface between the two metals.

Iredale studied [4] the parallelism between the effect of protective colloids on the catalytic decomposition of hydrogen peroxide and their efficiency as protective colloids. He found that the stronger a substance is as a protective colloid the greater its inhibitory power on catalytic activity. The order of inhibitive effect is gelatine and

[1] *Zeitsch. physikal. Chem.*, 1914, **88**, 414; Bancroft, Second Report, *J. Phys. Chem.*, 1923, **27**, 892.

[2] *J. Amer. Chem. Soc.*, 1920, **42**, 749.

[3] Second Report, *J. Phys. Chem.*, 1923, **27**, 894.

[4] *J. Chem. Soc.*, 1921, **119**, 109; 1922, **121**, 1536.

glue > egg albumin > gum arabic > sucrose, the last appearing not to affect the reaction at all. With gelatine the inhibitory effect was noticeable with one part of the protective colloid in twenty million parts of water. By determining the smallest amounts of different protective colloids which perceptibly retard the catalytic decomposition of hydrogen peroxide, Iredale obtained inhibition numbers which he then compared with the gold numbers, using gelatine as standard. The inhibition numbers for gelatine, egg albumin, dextrine, and starch were found to be 100, 20, and 0·33, while the gold numbers were correspondingly 100, 20, 0·66, and 0·40. Iredale therefore concluded that the inhibition number may be defined as the percentage of protective colloid, which is just insufficient to inhibit catalytic action. The ratios of these numbers for different protective colloids are of the same order of magnitude as the ratios of the gold numbers.

Rocosolano [1] found a similar relationship between the inhibitory action of gelatine and gum arabic. With sodium lysalbate the rate of decomposition of hydrogen peroxide in presence of colloidal platinum decreases to a minimum with increasing concentration of protective colloid, but passes through a minimum and then increases. This latter effect is to be attributed to the alkalinity of the protective colloid, which overcomes the inhibitory effect.

Bancroft [2] concludes that the essential difference between the "supported" and the "protected" catalyst is that in the former the platinum is on the outside of the asbestos, whereas the gelatine is on the outside of the platinum in the latter.

[1] *Compt. rend.*, 1921, **173**, 44, 234.
[2] *Colloidal Behaviour*, p. 274 (McGraw-Hill, 1924).

CHAPTER VI

CATALYST POISONS AND THE INHIBITION OF HOMOGENEOUS CHEMICAL REACTIONS

The phenomenon of "poisoning" is limited to contact catalytic reactions. The term "poisoning" was originally given to the reduction in activity of contact catalytic agents which is brought about by the presence of substances foreign to the reaction under study and present in relatively small amounts. The use of the term has been extended, and it is now recognised that poisoning to various degrees may occur, requiring relatively small or large amounts of a foreign substance, and, also, that even the reacting species or the resulting products may "poison" the reaction at the catalyst surface, slowing down the rate at which the process takes place.

The attention of the scientist to the phenomenon dates almost from the earliest studies of catalysis, as has been indicated in the historical introduction. Dobereiner's platinum "sickened" with use. Faraday investigated "some very extraordinary interferences" with the catalytic combination of hydrogen and oxygen in contact with platinum. Turner and Henry gave much attention to the phenomenon, and out of their researches developed methods of preferential catalytic combustion. The parallelism existing between the inhibition of contact catalysts and of enzymes probably led to the extended use of the term "poisoning" for the phenomenon.

The occurrence of poisoning in technical catalytic processes has been a determining factor in the industrial application of catalysis. The transfer of a catalytic process, perfectly practicable on the laboratory scale with purified materials, to the stage of technical production, in which materials of the same degree of purity are less easily obtained, is very frequently the central problem, determining ultimate success or failure. The early patent to Phillips on the oxidation of sulphur dioxide in presence of platinum only attained commercial exploitation when the problem of the removal of arsenical and other poisons from the sulphur gases was attained. All earlier commercial efforts to secure the catalytic production of sulphur trioxide failed, owing to poisons in the reacting gases. Volatile silicon

compounds lead to the poisoning of platinum in the ammonia oxidation process. Traces of sulphur compounds present in the reacting gases are poisonous in the ammonia synthesis reaction and in hydrogenation processes, with the normal catalysts for these operations. Oxides of sulphur and arsenic impair the activity of cuprous chloride catalysts in the Deacon chlorine process.

Classification.—Poisons may be either permanent or transitory. Thus the silicon compounds present in the ammonia-air mixture and in the oxidation of ammonia in contact with platinum gauze are oxidised to silica, which is deposited in part on the gauze and destroys its activity by covering up the platinum surface. The poisoning is permanent. Dust may also be included in the category of permanent poisons. Hydrogen sulphide and sulphur compounds transform an iron catalyst in ammonia synthesis and a nickel catalyst in hydrogenation processes to the corresponding sulphides, whose catalytic activity is negligible. The effect of the sulphur is cumulative and non-reversible, and it is necessary to regenerate a catalyst so poisoned by suitable means. In the case of an iron catalyst poisoned by sulphur, it is necessary to oxidise the sulphide completely to the oxide and then regenerate the metal by reduction. All cases of permanent poisoning require such a renewal of the contact mass before original activity is regained.

Transitory poisons are those which are only effective so long as they are present in the reacting system. After the removal of the harmful constituent from the reactants, provided the action has not been too prolonged, the original activity of the catalyst is restored. Faraday found that the inhibitory action of carbon monoxide on the platinum catalysis of hydrogen and oxygen only lasted so long as carbon monoxide is present in the reacting gases. Water vapour is a transitory poison in ammonia synthesis in presence of an iron catalyst, at a reaction temperature of 500° C. Low conversion efficiencies are obtained when the drying of the nitrogen-hydrogen mixture is incomplete. But the original activity is restored when thoroughly dried gases are turned into the reaction system.

It should be noted that the classification is dependent both on the catalyst and the reaction. A poison may be both transitory or permanent according to the catalyst used. In the case of ammonia synthesis, using uranium carbide (which changes to nitride with use) as catalyst, water vapour, oxygen, and carbon monoxide are permanent poisons. They convert the nitride to an irreducible uranium oxide, catalytically inert. It is this factor that has militated against the technical use of the otherwise very excellent uranium compound as a catalyst in ammonia synthesis. As already mentioned, water vapour is a transitory poison in ammonia synthesis with an iron catalyst. Furthermore, it is probable also that water vapour is the real poison in the case of oxygen and carbon monoxide poisoning in ammonia

LIBRARY

synthesis in presence of iron, since both these gases undergo quantitative transformation to water vapour and to methane and water vapour respectively under the conditions of the synthetic process.

The mechanism of poisoning.—It is now generally agreed that the inhibition of reaction produced by poisons is to be ascribed always to the diminution of the active catalyst surface by the poison. The reduction in surface may be mechanical and permanent, as in the illustrations of permanent poisoning already given. The reduction may also be temporary, and in this case it is brought about by preferential adsorption of the poison on the catalyst surface. Experimental data to illustrate this explanation of temporary poisoning have long been available, but it is only recently that the full realisation of their significance has been attained. Bancroft [1] has been especially instrumental in securing this recognition. His correlation of the literature has been supplemented by experimental data designed to give this point of view a quantitative basis.

Faraday's observation [2] that "the very power which causes the combination of oxygen and hydrogen is competent under the usual casual exposure of platina, to condense extraneous matters upon its surface, which, soiling it, take away for the time its power of combining oxygen and hydrogen, by preventing their contact with it", was extended by Henry.[3] He recognised that the presence of the reaction product might slow up the rate of reaction. He proved this by showing that the reaction rate between carbon monoxide and oxygen in contact with platinum was accelerated if the carbon dioxide produced was continuously removed from the reaction system by adsorption with caustic potash. Schönbein [4] pointed out that the hydrides of sulphur, selenium, tellurium, phosphorus, arsenic, and antimony were all active in retarding the reaction between air and hydrogen or ether in the presence of platinum. He was of the opinion that the inhibition was due to the formation of a film over the platinum, probably solid, not that of a gas film. This is not a necessary conclusion, as we now know that preferential adsorption may be strong, even of gases in minute concentrations, and an adsorbed gas film is just as effective in covering an active catalyst surface as a solid film. Maxted has shown,[5] however, that platinum or palladium may decompose hydrogen sulphide, the sulphur remaining on the surface, so that Schonbein's reasoning may be correct in certain cases.

Bredig's studies [6] of the analogy between colloidal metals and enzymes showed that the activity of colloidal platinum in the decomposition of hydrogen peroxide could be inhibited by minute amounts

[1] *J. Physical Chem.*, 1917, **21**, 767; *First and Second Reports, Committee on Contact Catalysis*, 1922, 1923.
[2] *Experimental Researches*, 353.
[3] *Phil. Mag.*, 1836 [3], **9**, 324.
[4] *J. pr. Chem.*, 1843, **29**, 238.
[5] *J. Chem. Soc.*, 1919, **115**, 1050.
[6] *Zeitsch. physikal. Chem.*, 1899, **31**, 258; 1901, **37**, 1, 323; *Ber.*, 1904, **37**, 798; *Zeitsch. Elektrochem.*, 1908, **14**, 51.

of foreign substances just as the function of enzymes in the same reaction could be similarly suppressed. Bancroft has compiled the following table relative to the effect of minute concentrations of substances as poisons in the decomposition of hydrogen peroxide by means of platinum and by hæmase, the active enzyme of the red blood corpuscles. In the second and third columns of the table are given the molar concentrations at which the poisons reduce the rate of decomposition to approximately one-half of the rate in absence of the poison.

Poison.	Colloidal Platinum.	Hæmase.
H_2S	M/300,000	M/1,000,000
HCN	M/20,000,000	M/1,000,000
$HgCl_2$	M/2,000,000	M/2,000,000
$HgBr_2$	..	M/300,000
$Hg(CN)_2$	M/200,000	M/300,000
I_2 in KI	M/5,000,000	M/50,000
NH_2OH . HCl	M/25,000	M/80,000
$C_6H_5NHNH_2$	..	M/20,000
$C_6H_5NH_2$	M/5,000	M/400
As_2O_3	M/50	No poisoning at M/2,000
CO	Very poisonous	No poisoning
HCl	M/3,000	M/100,000
NH_4Cl	M/200	M/1,000
NHO_3	No poisoning	M/250,000
H_2SO_4	,, ,,	M/50,000
KNO_3	,, ,,	M/40,000
$KClO_3$	Slight poisoning (?)	M/40,000

There is an undoubted parallelism between the two cases; since adsorption is specific, however, it is easy to understand that the same substances should not necessarily poison both platinum and hæmase; since, also, the extent of adsorption at a given concentration varies with the adsorbent, a given concentration of poison should not necessarily poison them both to the same extent.

The investigations of Meyerhof [1] on the "narcotic" action of alcohols and urethanes in the catalytic decomposition of hydrogen peroxide by platinum may also be cited in reference to the adsorption view. Ultramicroscopic evidence showed that the addition of the narcotics did not cause an agglomeration of the colloidal particles, and therefore the decreased rate of decomposition is not attributable to such cause. Meyerhof considers it probable that a surface film of the poison is formed over the catalytic agent, which prevents contact of the reacting substances with the catalyst. The retardation caused by alcohols and urethanes in the action of invertase on sugar is also attributed by Meyerhof [2] to displacement of the sugar from the surface

[1] *Pflüger's Archiv*, 1914, **157**, 307.
[2] *Pflüger's Archiv*, 1914, **157**, 251.

of the colloidal invertase. Cases of agglomeration of colloidal particles are, however, not unknown, as was pointed out by Bredig. [1]

The researches of Bodenstein and his co-workers on the kinetics of heterogeneous gas reactions demonstrated conclusively that both the reaction products and one or other of the reactants could act as poisons to the catalyst in the reaction. Fink's work with Bodenstein on the mechanism of sulphur dioxide oxidation [2] in contact with platinum established kinetically, as well as by experimental measurement of adsorption, that the sulphur trioxide produced inhibited the reaction by reason of its strong condensation on the surface of the platinum. This observation was incorporated in the Bodenstein-Fink theory of gas reactions at catalytic surfaces. The reaction velocity was assumed to be determined by the rate of diffusion of the reactant gases through a film of adsorbed resultant, which film was assumed to vary in thickness with the partial pressure of such resultant. Langmuir has shown,[3] however, that the kinetic data may receive a different explanation. If only unimolecular layers of adsorbed gas are possible—and Fink's measurements indicate the essential correctness of this view—the reaction rate is conditioned by the fraction of the surface which is bare of the strongly adsorbed gas under the experimental conditions. The strongly adsorbed gas may be one of the reactants, as the work of Bodenstein and Ohlmer [4] on the combination of carbon monoxide and oxygen in contact with quartz glass indicates. In this case, carbon monoxide is a poison to its own reaction. The experimental data are successfully interpreted by Langmuir in a manner analogous to that obtaining with sulphur trioxide. Bodenstein and Fink assumed that the surface of the glass was covered with an adsorbed layer of carbon monoxide of a thickness proportional to the pressure of the gas. By then assuming that the oxygen has to diffuse through the layer of carbon monoxide before coming into contact with the quartz glass where it reacts with the monoxide, it was possible to explain the fact that the reaction rate was proportional to the oxygen pressure and inversely proportional to the pressure of carbon monoxide. This naturally involves an assumption that the quartz glass is capable of adsorbing the gas in films many molecules deep. Bodenstein and Fink did not measure the adsorption of quartz glass for carbon monoxide. Some unpublished measurements by Benton indicate that the adsorption of this gas on quartz glass ground to almost colloidal dimensions is abnormally small, so small that the Bodenstein-Fink assumption is very improbable indeed. Even Langmuir's assumption that the surface is nearly covered with a layer one molecule deep seems to require some modification, namely, that only those portions of the quartz surface which are catalytically active are nearly covered with carbon monoxide. This would mean

[1] *Zeitsch. physikal. Chem.*, 1899, **31**, 332.
[2] *Zeitsch. physikal. Chem.*, 1907, **60**, 1.
[3] *J. Amer. Chem. Soc.*, 1916, **38**, 2286.
[4] *Zeitsch. physikal. Chem.*, 1905, **53**, 166.

that the " elementary spaces " of the surface are not all catalytically active. Langmuir's method of treatment would then be restricted to the " elementary catalytic spaces ". Further evidence for this idea of " elementary catalytic spaces " will be given in a succeeding section, when more quantitative evidence will be brought forward.

It is of interest to record that Bodenstein and Ohlmer showed that, in contact with crystalline quartz, the reaction between carbon monoxide and oxygen follows the ordinary stoichiometric equation. This result really requires further experimental test, as it involves a most interesting phenomenon. The carbon monoxide is apparently a poison with the fused quartz glass and not a poison with the crystalline variety of the same molecular species.

Adsorption by poisoned catalysts.—A number of isolated observations occur in the older literature concerning the influence of poisons on the adsorption, more generally designated the occlusive power, of catalytic agents. Berliner showed [1] that traces of fatty vapours from the air or from the grease on the stopcocks will decrease the occlusion of hydrogen by palladium from about nine hundred volumes to nothing. Mond, Ramsay, and Shields [2] showed that mercury vapour had the same action. Fink [3] demonstrated sulphur trioxide adsorption, but did not determine the adsorption of other constituents in its presence. Paal and Steger [4] showed that mercury vapour cuts down the adsorption of palladium hydrosol for hydrogen and decreases the catalytic activity towards oxy-hydrogen gas.

The most complete experimental study of adsorption in presence and absence of poisons has been carried out by Maxted,[5] who has demonstrated definitely the parallelism between the action of poisons on adsorption and on catalytic activity. The occlusive power of palladium for hydrogen in the presence of occluded hydrogen sulphide was shown to vary linearly with the content of inhibitant. The decrease in activity caused by the poisons, lead, mercury, zinc, sulphur, and arsenic, is directly proportional to the concentration of inhibitant from zero concentration in platinum up to that producing practically complete inactivity. The presence of lead decreases both the hydrogen adsorption by, and the catalytic activity of palladium. The amount of lead, as poison, required to reduce the catalytic activity to one-half, is very much less than that which reduces the occlusive power to one-half its original value. This may be explained by the fact that while occlusion is not confined to the surface, catalysis is mainly a surface phenomenon. It will be shown, however, that this observation, repeated with metals which show little or no occlusion such as palladium shows, leads to very interesting conclusions concerning the nature of

[1] *Wied. Ann.*, 1888, **35**, 903.
[2] *Zeitsch. physikal. Chem.*, 1898, **25**, 657.
[3] *Loc. cit.*
[4] *Ber.*, 1918, **51**, 1743.
[5] *J. Chem. Soc.*, 1919, **115**, 1050; 1920, **117**, 1280, 1501; 1921, **119**, 225, 1280; 1922, **121**, 1760.

catalyst surfaces and their reactivity. Maxted also studied the catalysis of hydrogen peroxide decomposition by platinum in solutions containing mercuric chloride, mercuric nitrate, and lead acetate. The curve obtained by plotting the catalytic activity of the platinum against the poison content is approximately linear until at least 70 per cent of the original activity has been suppressed. Preliminary experiments on adsorption indicated that inhibitants such as catalytically poisonous metals, in dilute solutions, are adsorbed strongly by platinum catalysts; but the adsorption is incomplete, except probably in the presence of relatively large concentrations of catalyst. This result has recently been quantitatively confirmed by Maxted.[1] It is worthy of note that arsenic, in the form of sodium arsenate, has a very low toxicity to platinum, whereas, in the form of arsine, it has a high activity as an inhibitant. This distinction was earlier noted by Bredig. It is a result which is entirely explicable on the basis of the newer theories with respect to the electronic configurations of arsine and arsenates.

Langmuir [2] showed that carbon monoxide was adsorbed tenaciously by platinum at room temperatures, and that at a temperature below 450° K. it should be impossible, in any reasonable time, to remove an adsorbed film of carbon monoxide merely by pumping off the gas with a good vacuum pump.[3] Taylor and Burns [4] confirmed this conclusion, working with platinum black, and found that it was necessary to burn the gas off with oxygen and then remove the excess oxygen with hydrogen. The hydrogen could then be removed by heating in a vacuum. When platinum black was not subjected to this treatment after having been exposed to carbon monoxide, but was merely evacuated at 110° C., a subsequent measurement of hydrogen adsorption showed three volumes at 25° C., whereas the true value on a clean surface was 6·85 volumes. This is a decrease of approximately 60 per cent. In an analogous way the adsorption of carbon monoxide itself at 110° C. declined from 19·2 volumes on a clean surface to 7·3 volumes when the surface had been exposed previously to carbon monoxide and then only evacuated. This would indicate that it is possible to render only about 40 per cent of the platinum surface free from carbon monoxide by heating the vessel to 110° C. in a vacuum of 0·002 mm. for a moderate period of time. This tenacity with which carbon monoxide is held and the diminished adsorption thereby produced is a convincing demonstration of the cause of inhibition noted by Harbeck and Lunge [5] when carbon monoxide was present in the hydrogenation of ethylene.

Taylor and Burns' catalyst was undoubtedly contaminated with stopcock grease and was not readily susceptible to exact adsorption

[1] *J. Chem. Soc.*, 1925, **127**, 73. [2] *J. Amer. Chem. Soc.*, 1918, **40**, 1398.
[3] *Trans. Farad. Soc.*, 1922, **17**, 641. [4] *J. Amer. Chem. Soc.*, 1921, **43**, 1283.
[5] *Zeitsch. anorg. Chem.*, 1898, **16**, 50.

measurements, since, if heated above 110° C., coalescence of the platinum black occurred. Pollard[1] obtained their results even more strikingly. With platinised asbestos kept very clean from grease, he obtained one hundred and sixty volumes of hydrogen adsorbed per volume of platinum. On introducing carbon monoxide, the hydrogen adsorption dropped to about seven volumes, which is practically negligible under the conditions of the experiment.

By studying the influence of poisons on the adsorptive capacity and catalytic activity of copper, Pease[2] avoided Maxted's difficulties with palladium, with which metal both surface phenomena, solution and compound formation with hydrogen may occur. Pease admitted mercury to a copper catalyst on which measurements were made both of adsorption and catalytic activity before and after poisoning. About 20 c.c. of mercury vapour (measured at 0° C. and 760 mm.) were admitted to the copper, which was then heated to 200° C. for one half-hour and evacuated. After cooling, the mercury had disappeared and the catalyst was unchanged in appearance. The adsorptions at 380 mm. pressure of hydrogen and ethylene, respectively, were found to be 3·25 c.c. and 8·55 c.c. before poisoning and 0·15 c.c. and 6·70 c.c. after poisoning. The rate of reaction was reduced to about one-half per cent of its value before poisoning. This reduction in rate is achieved with a reduction of hydrogen adsorption to about one-twentieth of its former value. The ethylene adsorption was only moderately diminished. This experimental evidence is conclusive in one respect. It indicates that the reactivity is not exactly proportional to the extent of the adsorbed gas. In other words, not all the adsorbed gas is rendered catalytically active in the process of adsorption.

Pease's subsequent work[3] has abundantly confirmed these conclusions and amplified them. Carbon monoxide, which is strongly adsorbed by copper, is a marked poison for the reaction between ethylene and hydrogen. By successively reducing the quantities of carbon monoxide introduced into the reaction system, Pease has shown that the carbon monoxide molecules required to render the reaction negligible under the conditions of the experiment are markedly less than the number of hydrogen molecules capable of being adsorbed by the copper catalyst. This seems to be quantitative evidence that only a fraction of the surface which is capable of adsorbing the hydrogen is capable of activating it sufficiently to promote reaction. It is apparently quantitative confirmation of a suggestion of Armstrong and Hilditch[4] and Rideal,[5] that an active catalyst is merely an average term expressing a surface on which a number of patches of maximum

[1] *J. Physical Chem.*, 1923, **27**, 370.
[2] *J. Amer. Chem. Soc.*, 1923, **45**, 1196, 2235.
[3] *Amer. Chem. Soc.*, Spring Meeting, 1924; Pease and Stewart, *J. Amer. Chem. Soc.*, 1925, **47**, 1235.
[4] *Trans. Farad. Soc.*, 1922, **17**, 670.
[5] *J. Chem. Soc.*, 1922, **121**, 314.

activity occur, the greater part of the surface being of quite a low order of activity.

The experiments of Maxted[1] on the poisoning of colloidal palladium for the hydrogenation of oleic acid had two similar conclusions. The falling off in catalytic activity on the addition of lead is found to be in direct proportion to the amount of lead adsorbed, over a wide range corresponding with the poisoning of the patches of maximum activity. Hydrogenation proceeds at a much slower rate on the less active portions to which the lead may be caused to adhere, but less strongly than on the active patches, thus necessitating a larger concentration of lead salt in solution. More detailed study of these cases is needed, and examples should be multiplied. It would be desirable to have not only data on adsorptions of the gases at various partial pressures, but also adsorptions of the gases from mixtures.

The work of Pease further indicates that from the study of poisons more may be learned with respect to the mechanism of activation and of adsorption. The work with mercury poisoning of the copper catalyst showed that the poisoning effect was most marked on the hydrogen and negligibly so on the ethylene. This indicates that reaction velocity is primarily dependent on the activation of the hydrogen. As the physical characteristics of the gas would suggest also, the slight influence of mercury poisoning on the ethylene adsorption tends to show that the adsorbed ethylene is largely present in condensed films, not in surface-unimolecular gas film complexes.

Progressive poisoning.—If a catalyst surface is composed of patches of varying activity it is evident that progressive poisoning of the surface ought to be attainable. With small amounts of a suitable poison the more highly activating centres of the surface will be rendered inactive. A reaction requiring high catalytic activity would cease after such poisoning, but one not requiring so active a catalyst might proceed. This phenomenon seems to have been realised in several cases.

One such case has been studied by Vavon and Husson[2] with the deliberate object of establishing the existence of progressive poisoning. The poisoning studied was that of platinum black by carbon disulphide. The authors showed that 5 grams of acetophenone in alcohol containing 0·2 gram of platinum fixed 25 c.c. of hydrogen on the average in six minutes. After the addition of 0·4 mg. of carbon disulphide no adsorption of hydrogen occurred. If, however, 1 gram of cyclohexene was then added to the solution, hydrogen was again taken up, 25 c.c. being fixed on the average in 4 minutes. In a second example a three-stage process of progressive poisoning was obtained. Five grms. of propyl ketone in 50 c.c. of glacial acetic acid containing 3 grms. of platinum showed a hydrogen adsorption of 25 c.c. in 4 minutes. The addition of 2·3 mg. of carbon disulphide stopped the adsorption. If 2 grms. of piperonal were now added to the solution, hydrogen

[1] *J. Chem. Soc.*, 1920, **117**, 1801; 1921, **119**, 1280. [2] *Compt. rend.*, 1922, **175**, 277.

absorption again commenced at a rate of 25 c.c. in 3·5 minutes. The further addition of 1·4 mg. of carbon disulphide again caused the hydrogen absorption to cease. The catalyst was still capable of some hydrogenation, for when 2 grms. of nitrobenzene were added to the solution the absorption of hydrogen again commenced, 25 c.c. being taken up on the average in 1·75 minutes. From this it may be concluded that nitrobenzene is readily reduced with practically inert catalysts. Propyl ketone needs an active catalyst.

This behaviour is very reminiscent of the observations of Sabatier [1] with reference to hydrogenation of the benzene nucleus with nickel. Sabatier showed that it required an active nickel catalyst, prepared by reduction at low temperatures, to effect the hydrogenation of the benzene nucleus. On the other hand, less active catalysts, prepared at higher reduction temperatures, while incapable of effecting the hydrogenation of the benzene nucleus, were nevertheless quite useful and efficient in the hydrogenation of the single ethylenic bond. The work of Gauger and Taylor,[2] already cited, showed that the higher temperature of reduction resulted in a catalyst of lower adsorptive capacity for hydrogen than one obtained by low temperature reduction. The effect of heat treatment of a catalyst is, therefore, quite analogous to the effect of poisoning. Pease confirmed this with experiments both on the reaction velocity of hydrogenation and the adsorptive capacity of copper for the gases hydrogen and ethylene. Pease writes: "In the course of the experiments on the catalytic combination of ethylene and hydrogen, the effect on both catalytic activity and adsorptive capacity of partially deactivating a copper catalyst by heating it to 450° in a vacuum was determined. The effect of deactivating this sample of copper by heating was in a general way similar to the effect of deactivating the sample by poisoning it with mercury. The curves have been moved over toward the pressure axis to nearly parallel positions, at the higher pressures at least. The heating has, however, decreased the hydrogen adsorption relatively less than the poisoning and the ethylene adsorption relatively more. Thus, at one atmosphere, the decrease in hydrogen adsorption amounts to 70 per cent, while the decrease in ethylene adsorption amounts to 22 per cent. These are to be compared with decrease of 92 per cent for hydrogen and 14 per cent for ethylene, caused by mercury poisoning. The absolute decreases at one atmosphere are 2·60 for hydrogen and 1·95 for ethylene. It will be seen that these figures are much more nearly of the same order than in the case of copper poisoned with mercury.

"The decrease in catalytic activity in the ethylene-hydrogen combination accompanying these decreases in adsorption amounted to 85 per cent. Just as in the case of the poisoning by mercury, one

[1] *Catalysis in Organic Chemistry*, Sabatier, translated by Reid (Van Nostrand, 1923).
[2] *J. Amer. Chem. Soc.*, 1923, **45**, 920.

must go to very low pressures to find a corresponding decrease in adsorption, indicating that it is the strong (low pressure) adsorption which is mainly responsible for catalytic activity."

Beneficial poisoning.—Since partial poisoning may be secured, it is evidently possible that use may be made of it to achieve certain reactions whilst obviating others. A very obvious application is in the case where a catalytic process proceeds too far with an active catalyst. By minimising the activity of such a catalyst or poisoning the more highly reactive patches with the requisite poison, the reaction may be stopped at the desired stage. Many investigations into the conditions necessary to secure a good yield of a desired product may, in reality, be unconscious applications of this procedure of beneficial poisoning. An example suggestive of this may be quoted.

Armstrong and Hilditch[1] have shown that in the catalytic dehydrogenation of ethyl alcohol in the presence of copper, the presence of water in the alcohol improves the yield of acetaldehyde relative to that of hydrogen. Thus, at 300° C., whereas anhydrous alcohol only gave an aldehyde-hydrogen ratio of 67 per cent, alcohol containing 8 per cent water gave a 95 per cent ratio. With the anhydrous alcohol, there is a marked increase in the yield of gaseous products, principally methane, carbon monoxide, and carbon dioxide, in addition to the hydrogen. It is evident that, with the anhydrous alcohol, secondary decomposition of aldehyde is much more pronounced than with alcohol containing water. Thus, methane and carbon monoxide result from one such secondary decomposition :

$$CH_3CHO \longrightarrow CH_4 + CO.$$

Evidently the water acts as a beneficial poison in that it poisons the catalyst for such secondary decompositions, which apparently require a larger energy of activation, in all probability as a result of strong preferential adsorption on the catalyst surface. Armstrong and Hilditch showed, by passing aldehyde vapour together with water over a copper catalyst, that the water had a considerable protective influence on the aldehyde.

The dehydrogenation of alcohol in the presence of nickel occurs at lower temperatures than in the presence of copper, but the secondary decomposition is very high. The data of Armstrong and Hilditch show that dehydrogenation occurred at 250° C. The aldehyde-hydrogen ratio was only 35·7 per cent and the evolved gas contained 60 per cent hydrogen, 20 per cent carbon monoxide, and 15-17 per cent methane. Evidently, in this case, the 8 per cent of water in the alcohol used was not sufficient to protect the aldehyde produced. It would be interesting to extend this study of dehydrogenation with nickel in the presence of water to see whether the secondary decomposition could be largely suppressed by increase of water content in the alcohol, since the low

[1] *Proc. Roy. Soc.*, 1920, 97A, 262.

yields obtained with copper at the higher temperatures could be partially restored by such an increase in water content.

Palmer's study [1] of this same reaction in the presence of a copper catalyst indicates that alcohol itself plays the same rôle as the water in the experiments already cited. He showed that, below 300° C., the secondary products were negligible when the dehydration of alcohol occurs; but, if a mixture of acetaldehyde and hydrogen is passed over the copper catalyst between 250° and 300° C., much of the aldehyde is decomposed. Bancroft has suggested [2] that such cases might be called "protective poisoning".

The same procedure was used during the years 1917–1919 for the production of ethylene from alcohol in presence of kaolin. Instead of a low temperature process, the reaction was conducted at red heat and the products were protected from decomposition by using alcohol-water mixtures, even though the process was dehydration.

The researches of Rosenmund, Zetsche, and Heise [3] have shown that partial poisoning may be used to attain new organic preparations and to manipulate a given reaction to yield various desired end products. Thus, if benzoyl chloride is dissolved in pure benzene and then reduced by hydrogen in presence of colloidal palladium, practically no benzaldehyde is produced. If, instead of pure benzene, ordinary benzene be used, a good yield of benzaldehyde is obtained. This indicates the presence in ordinary benzene of a substance or substances which poisons the reduction of benzaldehyde to benzyl alcohol. That the poisoning is due to the sulphur compounds in ordinary benzene seems probable from the fact that additions of sulphurised organic compounds to pure benzene produced like effects. Quinoline, quinoline heated with sulphur giving an impure thioquinanthrene, purified thioquinanthrene, xanthone, and dimethylaniline were all employed as beneficial poisons. Thus, the addition of 1 mg. of thioquinanthrene to a system containing 2 grms. of benzoyl chloride and 0·7 grm. of palladium in 10 c.c. of xylene, gave a yield of 78 per cent of benzaldehyde when reduction was carried out at 150° C. Impure thioquinanthrene under the same circumstances gave a 90 per cent yield. If, instead of the sulphurised quinoline, 0·1 grm. of distilled quinoline was added to the xylene, practically no benzaldehyde was obtained, reduction to the benzyl alcohol stage occurring. The addition of xanthone to the reaction mixture promotes reaction between unchanged benzoyl chloride and benzyl alcohol with the formation of benzyl benzoate. This ester is the principal product when toluene is used as solvent in place of xylene. In toluene, reduction of benzyl benzoate by hydrogen to toluene and benzoic acid does not readily occur, whereas, in xylene, this further reduction occurs freely. Thus, with palladium partially poisoned in a variety of ways, the reduction of benzoyl chloride

[1] *Proc. Roy. Soc.*, 1920, 98A, 13. [2] *First Report, Committee on Contact Catalysis.*
[3] *Ber.*, 1921, **54**, 425, 638, 1092, 2033, 2038.

by hydrogen may be directed to yield, in the main, one or other of the substances benzaldehyde, benzyl alcohol, benzyl benzoate, dibenzyl ether, or toluene, the product obtained being determined by the nature and amount of the added substance.

Zetsche has extended the work to the catalytic dehydrogenation of alcohols, with accompanying oxidation of the hydrogen produced, by passage of air through the solution. With copper as a catalyst, the yield of benzaldehyde from benzyl alcohol dissolved in cymene is increased when quinoline is added to the solution. Addition of nitrobenzene still further increases the yield. There is a possibility that in this case there is a coupled catalytic reaction, dehydrogenation of the alcohol and reduction of the nitro-compound. Nickel and silver as catalysts are also more efficient when quinoline is present, but, with these metals, benzyl ether and resins are produced. Much more detailed study of these cases is needed before a complete understanding of the particular mechanisms can be attained.

The vapour phase dehydrogenation of methyl alcohol to yield formaldehyde is probably also an additional case in which beneficial poisoning may occur. As is well known there is a considerable tendency for the formaldehyde produced to undergo secondary decomposition to carbon monoxide and hydrogen. Low yields are frequent in the technical operation. Steam may in this case be used as a protective poison.

Rate of adsorption and poisoning.—In catalytic gas reactions the normal time of contact of the flowing gases with the catalytic material is of short duration. Thus, in the case of ammonia oxidation with a platinum gauze catalyst, the time of contact is of the order of a hundredth of a second. With such brief periods of contact it is evident that any decrease in the rate of adsorption will have a corresponding effect on the velocity of reaction.[1] It is well known that the attainment of equilibrium in adsorption from a mixture of gases is markedly longer than from a single gas. It is evident, therefore, that the effect of catalyst poisons may be due in part to a reduction in the velocity with which adsorption of the reacting substances occurs. No experimental data on this point are available, but certain figures in connection with charcoal adsorptions give the idea some support. Harned[2] has shown that the rate of adsorption of chloropicrin by a charcoal the surface of which has been cleaned by washing with chloropicrin, is much greater in the initial stages of adsorption than is the case with a charcoal which has not been so cleaned, although the final equilibrium is apparently about the same in the two cases. Patrick and his co-workers[3] have shown that the hysteresis shown in the adsorption curves of gases on silica gel is to be attributed to the influence

[1] Taylor, *Trans. Amer. Electrochem. Soc.*, 1919, **36**, 149.
[2] *J. Amer. Chem. Soc.*, 1920, **42**, 372.
[3] *J. Amer. Chem. Soc.*, 1920, **42**, 946; *J. Physical Chem.*, 1925, **29**, 601.

of gaseous impurities on the velocity of adsorption of the gases being studied.

Poisoning and poison concentration.—The data of Maxted, already cited (p. 133), show a linear proportionality over a considerable range for gaseous poisons adsorbed on the catalysts from gases containing small amounts of gaseous poison. These results are readily understandable, since, for very low gas pressures, the adsorption of a gas is essentially proportional to the gas pressure.

In those cases in which the poison concentration attains much higher values such simple relations will not hold. Thus, in the experiments of Bodenstein and Fink, the velocity of sulphur trioxide formation from sulphur dioxide and oxygen varies inversely as the square root of the sulphur trioxide concentration. In the reaction of carbon monoxide-air mixtures at quartz surfaces the reaction velocity is inversely proportional to the carbon monoxide concentration. Langmuir has shown[1] that special considerations as to the spaces occupied on the surface by the several gases may be adduced to indicate the observed reaction mechanism. In general, the reaction mechanism is determined by the distribution of the reactants and poisons between the gas phase and the surface layer of the contact mass. This distribution will be by no means constant as to the distribution of the poison with wide variations in the reactant concentrations. Hence, a varying reaction kinetics for one and the same reaction at different stages of the process in presence of a poison can be anticipated. The data of Bodenstein and his co-workers on the kinetics of heterogeneous reactions give abundant illustrations of this fact. The distribution between the gas phase and the surface may also be influenced by the nature of the surface, its concentration of active patches. This leads to the intriguing possibility that, by suitable preparation of the catalyst surface, the deleterious effect of poisons may be minimised, a result which would have considerable technical importance.

Poisoning and temperature.—Since temporary poisoning is generally due to adsorption on the surface of the catalyst, and since adsorption is, in general, an exothermic process, it is evident that, with rise in temperature, the fraction of the surface which is covered with poison at any given partial pressure of the poison will decrease. The catalytic efficiency of the surface will therefore increase at a greater rate than is the case if no poisoning is present. For, in addition to the normal increase in reaction velocity with temperature, there will be the increase due to increase in available surface. The temperature coefficient of a catalytic reaction poisoned by a temporary poison will, therefore, be larger than that of the normal catalytic reaction. This point has been indicated by W. C. McC. Lewis.[2] It holds true whether the resultants of the reaction or a body foreign to the reaction is the

[1] *J. Amer. Chem. Soc.*, 1916, **38**, 2263. [2] *J. Chem. Soc.*, 1919, **155**, 182.

poisoning constituent, provided the poisoning is attributable to a reversible adsorption. If one of the reactants is responsible for the poisoning effect, the variation of reaction velocity with temperature will depend on the extent to which the surface is covered with the reactant poison. With the active surface almost completely covered with this poison a high temperature coefficient will result. As the temperature rises and the surface covered by poison becomes less and less, the conditions will change towards a state in which the adsorbed poison behaves more and more as an ordinary constituent of the reaction process—it ceases to be a poison.

There are few quantitative measurements which can be cited in support of these observations ; there are, however, numerous qualitative observations which substantiate the conclusions. Thus, the inhibitory influence of water vapour, oxygen, and carbon monoxide on the synthesis of ammonia from its elements in contact with iron catalysts becomes progressively less important as the temperature rises. Dougherty and Taylor [1] showed that the poisoning effect of carbon monoxide on the vapour phase hydrogenation of benzene in presence of nickel was pronounced at 100° C., but became less effective as the temperature was raised.

Permanent poisons, since they completely destroy the catalytic activity of the surface they cover, do not produce any abnormality in the temperature coefficient. Their effect is to decrease the extent of surface, to a degree independent of the temperature of operation of the catalyst.

Poisoning and apparent equilibria.—Bancroft has pointed out [2] that, in the case of a reaction poisoned by one of the products, the apparent equilibrium attained will depend on the quantity of catalytic agent employed. If there is a large excess of catalytic agent, the reaction will run to an end or true equilibrium before the catalyst is entirely poisoned. If, on the other hand, there is only a small amount of catalytic agent it will very soon be poisoned and we shall have an apparent equilibrium reached from only one side, which will vary with the amount of catalyst used. As an example of such a case, Bancroft cites the work of Neilson [3] on the splitting of salicin and amygdalin by platinum black. In the former case the salicylic acid produced, and, in the latter case, the hydrocyanic acid produced, are toxic to the platinum. If means were taken to ensure removal of the hydrocyanic acid formed, Neilson found that the splitting of the amygdalin proceeded further than in the absence of such precautions.

This effect of poisons on equilibrium should be quite marked with enzyme catalysts. In such cases there is the possibility that not only adsorption of poisons may occur but also agglomeration of the enzymes

[1] *J. Physical Chem.*, 1923, **27**, 548.
[2] *First Report, Committee on Contact Catalysis*, 1922.
[3] *Amer. J. Physiol.*, 1906, **15**, 148.

as a result of the action of reaction products. Apparent equilibria will result dependent on the amount of enzyme used. This has already been observed.[1]

The Inhibition of Homogeneous Chemical Reactions

Catalysis is concerned, in the main, with the acceleration of reactions occurring with diminution of free energy. The catalyst may be distributed molecularly in a homogeneous reaction system or it may be an interface in a heterogeneous system. In the latter case, the catalytic efficiency of the surfaces may, as we have shown, be diminished by the effect of poisons concentrated thereon. In homogeneous systems, where the catalyst is molecularly dispersed, a retardation suffered by the reaction system is not usually regarded as a case of poisoning, though the effect produced may, as we shall see, involve a mechanism very similar to that involved in the poisoning of an active centre in a heterogeneously distributed catalyst. It has been usual to characterise such cases of retardation in homogeneous reactions by the term "negative catalysis". For several reasons the term is not very suitable and it seems preferable to group the many phenomena included in the study under the more inclusive title, inhibition of homogeneous chemical reactions.

Catalytic reactions occur when the change from an initial set of reactants to a final set of resultants occurs more readily in presence of the catalyst than in its absence. In homogeneous systems it has been shown that this necessarily involves some association between reactants (A) and catalyst (C), whereby the products (B) result more readily from the associated complex or compound (A : C) than from the reactants (A) alone. The case strictly parallel to this involving retardation, implies an association between A and C such that the product B is less readily produced. If the association assumed involved a very considerable diminution in the active mass of A, it is evident that a retardation would result. It is evident, however, that this is by no means the only way in which retardation of reaction may occur. If the reaction A to B be catalysed by the presence of a powerful catalyst X, then the addition of anything which will decrease the concentration of X in the reacting system will effect a retardation of the observed reaction process. It has been shown also in the discussion of the energy of activation of chemical processes (Chapter III.) that the possibility exists of the energy produced by chemical reaction being transferred in some manner or other to reactant molecules, thereby activating them and causing a sequence or chain of reactions. Any substance, added to a reaction system in which such a chain mechanism is possible,

[1] Tammann, *Zeitsch. physikal. Chem.*, 1895, **18**, 426; Kastle and Loevenhart, *Amer. Chem. J.*, 1900, **24**, 491; Bancroft, *J. Physical Chem.*, 1918, **22**, 39.

and causing the length of the chains which occur to be shortened, will effect a retardation of the reaction velocity. It is with a variety of retarded chemical processes, involving one or other mechanism such as those just outlined, that the present section on the inhibition of homogeneous chemical reactions will deal.

Historical.—Though less assiduously studied, examples of inhibition have been recognised almost as long as examples of catalytic acceleration. Thènard,[1] in his investigations of hydrogen peroxide, found both catalysts and inhibitors for the decomposition of this substance. He showed that the peroxide was stable in acids, but underwent rapid thermal decomposition in presence of alkalis. The inhibitory power of oxygen on the photochemical combination of hydrogen and chlorine was early ascertained and received quantitative study in the classical researches of Bunsen and Roscoe.[2] It will be shown that this is one of many such inhibitions of photochemical processes, including the inhibition of the photochemical decomposition of hydrogen peroxide. The study of reaction kinetics in the early days of the development of physical chemistry provided numerous examples of inhibition susceptible to quantitative study. The influence, on the hydrolytic activity of weak acids, of neutral salts having a common anion was a very striking example of the inhibition of a catalysed reaction. The researches of Müller[3] on the inhibitory power of hydrobromic acid in the hydrolytic decomposition of bromo-succinic acid provided a good example of auto-inhibition or auto-retardation. The researches of Bigelow[4] on the inhibitory power of such substances as mannite, benzaldehyde, and benzyl alcohol on the rate of oxidation of sodium sulphite solutions by dissolved oxygen initiated quantitative investigations of the inhibitory power displayed in a wide variety of autoxidation processes. It is in the prevention of autoxidation and in the preservation of hydrogen peroxide that the principal technical applications of inhibition have been made. Water has been shown to function as inhibitor in a number of reactions occurring in non-aqueous solvents. Bredig and Lichty[5] investigated the retarded decomposition of oxalic acid in concentrated sulphuric acid solutions when minute amounts of water are added. Water similarly inhibits the conversion of acetophenoxime to acetanilide in sulphuric acid solutions,[6] and also the decomposition of triethyl sulphine bromide[7] in acetone and acetic acid solutions. The most important example, however, of the inhibitory power of water is in its action on the esterification of organic acids in alcoholic solutions, as investigated by Goldschmidt and his co-workers[8] and by

[1] *Ann. Chim. Phys.*, 1818, **9**, 314.
[2] *Pogg. Ann.*, 1855, 96; 1857, 100; 1857, 101; 1859, 108.
[3] *Zeitsch. physikal. Chem.*, 1902, **41**, 483. [4] *Zeitsch. physikal. Chem.*, 1893, **12**, 329.
[5] *Zeitsch. Elektrochem.*, 1906, **12**, 450; *J. Physical Chem.*, 1907, **11**, 256.
[6] Lobry de Bruyn and Sluiter, *Proc. Akad. Wetenschap Amst.*, 1904, **6**, 773.
[7] V. Halban, *Zeitsch. physikal. Chem.*, 1909, **67**, 129.
[8] *Ber.*, 1895, **28**, 3218; 1906, **39**, 711; *Zeitsch. Elektrochem.*, 1906, **12**, 432.

Lapworth and his students.[1] In the decomposition of diazo-esters in alcohol,[2] water is also an inhibitor.

Classification.—It is difficult, in the absence of any well-defined body of scientific opinion as to the precise mechanism of inhibitory action, to adopt a completely satisfactory classification of inhibited reactions. Tentatively, however, it seems desirable to base a system of classification on the several mechanisms which have already been offered in explanation of the phenomena, and to discuss the more important individual examples of each type in some detail. The inhibited reactions may be discussed under the following headings :

(*a*) Reactions inhibited by reduction of the concentration of a positive catalyst.

(*b*) Reactions inhibited by reduction of the concentration of a reacting constituent.

(*c*) Reactions inhibited by diminution of a chain of reactions in which activating energy is produced.

It will not be possible in every case to assign a given inhibition with certainty to one or other of these classes. Other classes of inhibition may also be required. Experimental work is needed before such can be accomplished.

Reactions inhibited by reduction of the concentration of a positive catalyst.—This class was formerly the most important class of inhibited reactions. It was definitely established by the work of Titoff [3] on the rate of oxidation of sodium sulphite solutions by dissolved oxygen. Bigelow [4] and Young [5] had shown that a bewildering variety of chemical agents diminished the rate of oxidation of such substances. Titoff was able to show that the presence of extremely minute amounts of foreign substances, for example 10^{-13} molar copper sulphate, was sufficient to produce a perceptible acceleration of the rate of oxidation of such solutions. Luther is credited by Titoff with the conclusion, from a quantitative study made by the latter, that the function of the inhibitor was to suppress these powerful positive catalysts and so retard reaction. Titoff found that the rate of reaction was inversely proportional to the concentration of inhibitor, I. He attributed this to the formation with the catalyst, C, of an inert complex, IC, whence, by the law of mass action, for the process :

$$I + C \rightleftarrows IC,$$

$$[C] = K\frac{[IC]}{[I]}.$$

The square brackets denote concentrations, and K is the mass action

[1] *J. Chem. Soc.*, 1908, **93**, 2167, 2187.
[2] Bredig and Frankel, *Zeitsch. physikal. Chem.*, 1907, **60**, 202.
[3] *Zeitsch. physikal. Chem.*, 1903, **45**, 641.
[4] *Zeitsch. physikal. Chem.*, 1898, **26**, 493.
[5] *J. Amer. Chem. Soc.*, 1901, **23**, 119, 450 ; 1902, **24**, 297.

constant. If the measured rate of reaction be proportional to [C] it will also be proportional to $\frac{[IC]}{[I]}$, and, therefore, inversely as [I] so long as [C] is small compared with [I], or, alternatively, so long as the concentration of complex [IC] is relatively large, for then [IC] can be regarded as constant.

Titoff found in the enormous sensitivity of reactions to minute amounts of accelerating catalysts a ready explanation for the extremely small amounts of inhibitors which were found, in the studies of Bigelow, Young, and Titoff, to be adequate for the inhibition of reaction. Titoff's explanation became, consequently, the most quoted explanation of inhibition. While it is undoubtedly true that such a mechanism will yield the observed inhibitory reaction, it is also certain that Titoff's explanation may not be the only reason for inhibitory action even in the particular case of sodium sulphite oxidation; nor is it the only explanation for the minute amounts of inhibitor required. It will be shown in other sections that further possibilities exist. Such possibilities might even be forecast from the variety of inhibitors found for the reaction. On Titoff's view, one would be compelled to assume a very varied series of complexes between the active catalyst, say the copper ion, and the inhibitors studied.

The inhibitory power of water in the esterification of acids in alcoholic solutions and in the decomposition of diazo-esters in alcoholic solutions, as well as the well-known action of neutral salts of weak organic acids on the hydrolysis of esters in aqueous solutions in presence of the corresponding weak organic acids, probably all represent complex cases of the Titoff type of inhibition. In these reactions the hydrogen ion, in one or other form, either non-hydrated (Lapworth) or alcoholated (Goldschmidt), is a positive catalyst for the reaction. The changes in ionisation and in the extent of hydration or solvation due to the addition of the inhibitor are the complex factors in these cases. They are dealt with in detail in appropriate sections of this book.[1]

The inhibitory power of water on the decomposition of oxalic acid in concentrated sulphuric acid solutions [2] and on the conversion of acetophenoxime to acetanilide [3] in the same solvent, may also be attributed to the removal of a positive catalyst, in this case sulphur trioxide, from the solution by interaction with the added water. The former of these two cases has been particularly well examined from the standpoint of reaction kinetics. This mechanism of inhibition is in agreement with the observation that when 0·05 per cent of water is added at 25° C. the time required to secure the decomposition of oxalic acid increases to over sixfold of that required when no water has been added, and that when the amount of water reaches 0·1 per

[1] See p. 160 *et seq.*

[2] Bredig and Lichty, *Zeitsch. Elektrochem.*, 1906, **12**, 450; *J. Physical Chem.*, 1907, **11**, 255.

[3] Lobry de Bruyn and Sluiter, *Proc. Akad. Wetenschap Amst.*, 1907, **6**, 773.

cent the time is increased nineteenfold. It is also in agreement with the influence of temperature on the inhibitory power, this decreasing as the temperature rises, and is also in agreement with the abnormal temperature coefficient of the reaction, 4·42 at 25° C. and 3·35 in the interval 70°-80° C. This high coefficient is to be attributed to the joint operation of two factors, the increase of the concentration of SO_3 catalyst with increase of temperature and the ordinary increase in efficiency of the catalyst with temperature. Bredig and Lichty showed that alkali sulphates also retard the decomposition. Since these form double compounds with sulphuric acid they would also tend to suppress sulphur trioxide in the acid solution.

All [1] of these facts are in agreement with the assumption that the inhibition is attributable to compound formation between activated molecules of sulphuric acid and the water molecules as an alternative reaction to compound formation between the active sulphuric acid molecules and oxalic acid, which may be regarded as the preliminary stage in the oxalic acid decomposition. The alkali sulphate would behave similarly. Making use of compound formation as a criterion of inhibitory power, Taylor found [2] that acetic acid and dimethyl pyrone both behaved as inhibitors of oxalic acid decomposition. If this mechanism were the correct one, the inhibitions would fall among those in which the reactant rather than the catalyst was removed by the inhibitor. That the function of the water might be the removal of catalytic sulphur trioxide appears more probable to Christiansen,[3] who points out that it is supported by the observation that decomposition of oxalic acid is very rapid in sulphuric acid to which sulphur trioxide has been added.

A recent research by Whitford [4] on the decomposition of malic acid in sulphuric acid solutions, and a comparison of the results obtained with the earlier work of Lichty on oxalic acid and the researches of Schierz [5] on formic acid, lends some support to Taylor's theory. Sodium, potassium, and silver sulphates, water, dimethyl pyrone, and acetic acid are all found to exert an inhibitory action in the order which the mechanism of compound formation would forecast; that is to say, it is greatest with the sulphates and least with acetic acid. Sulphur trioxide in small concentrations has no effect; in large concentrations it inhibits the reaction, both results contrary to what one would expect on Christiansen's view that the activity of sulphuric acid is to be attributed to its sulphur trioxide concentration. The relative effect of water on the rate of decomposition of oxalic, malic, and formic acids in sulphuric acid is also in agreement with the theory, being most marked with the strongest acid, oxalic acid, and least with formic acid. Furthermore, as with oxalic acid, the temperature

[1] *J. Physical Chem.*, 1923, **27**, 322.
[2] Unpublished experiments.
[3] *J. Physical Chem.*, 1924, **28**, 145.
[4] *J. Amer. Chem. Soc.*, 1925, **47**, 953.
[5] *J. Amer. Chem. Soc.*, 1923, **45**, 447.

coefficient of the reaction rate is abnormally large, the average value being 3·72 for a ten-degree interval from 20° to 50°.

Reactions inhibited by reduction of the concentration of a reacting constituent.—It is quite possible to formulate a series of general cases in which inhibitions by reduction of the concentration of a reactant shall occur. Thus, for example, in any reaction in which one of the actual reactants in the process is the ion of an electrolyte, the undissociated electrolyte being either non-reactive or of a lower order of activity than the ion, inhibition will occur whenever any substance is added to the reaction system which represses the dissociation of the electrolyte whose ion is reactive. Conversely, in any reaction in which the undissociated electrolyte is more reactive than its ions, inhibition will occur when, to the reaction system, substances are added which will increase the dissociation of the electrolyte. If in a reaction of either type just discussed the inhibitor results from the reaction, the system will show auto-inhibition or auto-retardation. Examples of these several types are well known and have been comprehensively studied with respect to reaction kinetics.

Müller [1] studied the inhibitory action of hydrobromic acid on the hydrolysis of bromo-succinic acid. Since the hydrogen bromide results from the hydrolytic process, this represents an example of auto-inhibition. Müller showed that the equation

$$dx/dt = k\frac{a-x}{x}$$

more nearly represented the effect of the concentration, x, of the inhibitor, on the rate of reaction, than does an equation formulated by Ostwald for an auto-inhibited process :

$$dx/dt = k_1(a-x) - k_2x(a-x).$$

That this expression of Ostwald cannot be generally applicable is evident from the observation that, with certain values for k_1 and k_2, the value of dx/dt would change sign; that is, the reaction become zero, or would even reverse itself—which has never been observed.

Senter and Porter,[2] dealing with the influence of the hydrogen halides on the hydrolysis of the several halogen acids of acetic, propionic, and butyric acids, with the inhibitory action of nitric acid on the reaction between bromo-substituted aliphatic acids and silver nitrate in alcoholic solutions, and with the problem of inhibition in general, showed that the term involving the inhibitor concentration normally appeared in the denominator. They showed that, in the reactions of the halogen-substituted acids with water, both the undissociated molecule and the anion of the acid undergo hydrolysis at rates definite and distinct for each acid and each ion. Retardation is produced by the halogen acid formed, in those cases in which the rate of hydrolysis

[1] *Zeitsch. physikal. Chem.*, 1902, 41, 483. [2] *J. Chem. Soc.*, 1911, 99, 1049.

of the ion is faster than that of the undissociated molecule. This is the case, for example, with bromo-propionic anion and acid. The inhibition is, therefore, due to the function of the strong hydrogen halide in altering the relative ratios of the more active anion and the less active molecule of the weak acid. They developed the mathematical equations expressing this explanation and showed that the concentration of inhibitor appeared in the denominator of the equations, in agreement with their experimental observations.

The inhibitory power of water on the velocity of decomposition of triethyl sulphine bromide in acetone and to a less degree in acetic acid solutions, may be explained on the assumption that the addition of water increases the dissociation of the bromide in the solvent. If the undissociated molecule alone undergoes decomposition, then the mechanism of the inhibitory power is manifest. This assumption should be tested. Furthermore, it should be noted that this reaction also shows a high temperature coefficient of 3 per 10° rise in temperature with a water concentration as high as 6-7 per cent. The reaction also shows an exponential increase in the effect of the concentration of water on the reaction velocity. These observations must be accounted for in a completely satisfactory explanation of this inhibition.

A well-known case of inhibition, namely the inhibitory power of hydrogen bromide and of iodine, on the thermal and the photochemical combination of hydrogen and bromine, first studied in detail by Bodenstein and Lind,[1] has recently been elucidated. It furnishes a further example of a reaction inhibited by diminution of the concentration of one of the reacting species. Bodenstein and Lind showed by a study of the kinetics of the thermal combination that the rate of formation of hydrogen bromide could be represented by an equation of the form

$$\frac{d[2HBr]}{dt} = \frac{k[H_2]\sqrt{[Br_2]}}{m + \dfrac{[2HBr]}{[Br_2]}},$$

where the square brackets indicate concentrations of the several reacting species. The form of the equation clearly shows the inhibitory influence of the hydrogen bromide formed. The explanation of this singular equation was suggested, approximately simultaneously, by Christiansen,[2] Polanyi,[3] and Herzfeld.[4] These three investigators assumed that the initial action was a dissociation of bromine into atoms :

$$Br_2 = 2Br. \quad . \quad . \quad . \quad . \quad . \quad (i.)$$

[1] *Zeitsch. physikal. Chem.*, 1906, **57**, 168.
[2] *Dansk. Vid. Math. Phys. Medd.*, 1919, **1**, 14.
[3] *Zeitsch. Elektrochem.*, 1920, **26**, 50.
[4] *Zeitsch. Elektrochem.*, 1919, **25**, 301 ; *Ann. Physik*, 1919 (4), **59**, 635.

By collision of such a bromine atom with a hydrogen molecule, reaction occurred occasionally thus:

$$H_2 + Br = HBr + H. \quad . \quad . \quad . \quad . \quad (ii.)$$

The resulting hydrogen atoms could disappear in two ways:

$$H + Br_2 = HBr + Br \quad . \quad . \quad . \quad . \quad (iii.)$$

and

$$H + HBr = H_2 + Br. \quad . \quad . \quad . \quad . \quad (iv.)$$

Finally, the bromine atoms, which would otherwise accumulate and produce an ever increasing reaction velocity, must maintain themselves in a stationary state by reason of the reverse reaction to (i.)

$$2Br = Br_2.$$

Such a sequence of reactions gives a kinetic equation of the form obtained by Bodenstein and Lind. On this basis, the inhibitory power of the hydrogen bromide is to be attributed to its capacity to remove hydrogen atoms from the reaction system, these hydrogen atoms being producers of hydrogen bromide by reaction (iii.). The inhibitory power of iodine is similarly explained as due to the reaction

$$H + I_2 = HI + I,$$

the iodine atoms being too inert to bring about reactions similar to those between bromine atoms and hydrogen.

This theory of the mechanism of the inhibitory action of hydrogen bromide and iodine, together with the observation of light sensitivity of the hydrogen-bromine reaction at higher temperatures, has led Bodenstein and his co-workers [1] to renewed study of the reaction process. The interesting conclusion from this work is that bromine atoms are by no means so reactive as has been postulated in recent theories of reaction mechanism. Bodenstein and Lütkemeyer [2] conclude that only 1·25 per thousand of the collisions between bromine atoms result in the formation of bromine molecules.

Reactions involving a chain mechanism and showing inhibition phenomena.—*The hydrogen-chlorine combination.*—The photochemical combination of hydrogen and chlorine is the best known example of this class of phenomena. As has long been known, the photo-reaction of the two gases is enormously sensitive to traces of impurities. In this respect ammonia and nitrogenous organic bodies are especially powerful inhibitors of reaction. Special precautions to remove such impurities are necessary if a sensitive reaction mixture is to be obtained.[3] Oxygen, however, forms a very efficient inhibitor of the

[1] *Zeitsch. Elektrochem.*, 1924, **30**, 416; *Zeitsch. physikal. Chem.*, 1924, **114**, 208.

[2] *Zeitsch. physikal. Chem.*, 1924, **114**, 208.

[3] See Chapman and Burgess; Chapman and MacMahon, *J. Chem. Soc.*, 1906, **89**, 1402; 1909, **97**, 845; or, for a concise summary, *Treatise on Physical Chemistry*, chap. xviii. pp. 1218-1228 (Macmillan & Co., 1924).

reaction, and its influence has been studied kinetically by several workers since the original classical investigations of Bunsen and Roscoe.[1] It has been shown that the rate of the hydrogen-chlorine combination is approximately inversely proportional to the amount of oxygen present in the reaction mixture.

By comparing the light energy absorbed by the system with the chemical energy produced as a result of the light absorption, Bodenstein showed,[2] in 1913, that there was an enormous divergence between the two quantities in a sensitive gas mixture. Thus, Bodenstein calculated that, in his most sensitive mixture, for every quantum ($h\nu$) of light energy absorbed, as many as 10^6 molecules of chlorine were caused to react. This large divergence from expectations based upon Einstein's Law of the Photochemical Equivalent,[3] according to which there should be equivalence, in pure photo-reactions, between light energy absorbed and chemical energy produced, led to a number of theories[4] to account for the excessive amount of reaction produced by the light. Of these, the most popular has been that of Nernst, which, although far from being completely satisfactory as an explanation of all the facts of the photochemical combination of hydrogen and chlorine,[5] nevertheless illustrates well the idea of a chain of reactions and has led to a more detailed study of reactions, which deviate widely from the Einstein Law of the Photochemical Equivalent. Nernst assumed that the initial absorption of light resulted in a dissociation of a chlorine molecule into atoms:

$$Cl_2 + h\nu = 2Cl.$$

These chlorine atoms were then able to enter a series or chain of reactions, each reaction occurring with free energy decrease and therefore spontaneous, whereby, in each, hydrogen chloride and either hydrogen or chlorine atoms were produced:

$$Cl + H_2 = HCl + H,$$
$$H + Cl_2 = HCl + Cl.$$

Such reactions continued until the hydrogen and chlorine atoms were lost either by recombination with each other or in some other manner.

It is easy to show that such a mechanism cannot have general applicability. It breaks down, for example, when we come to consider various other halogenation processes in which a similar disparity exists

[1] See, for example, *J. Chem. Soc.*, 1909, **97**, 845; 1919, **115**, 1264; 1923, **123**, 3062; *Zeitsch. physikal. Chem.*, 1913, **85**, 297.

[2] *Zeitsch. physikal. Chem.*, 1913, **85**, 351.

[3] *Ann. Physik*, 1912, **37**, 832; *Verh. Deut. Physikal. Ges.*, 1916, **18**, 315.

[4] *Zeitsch. Elektrochem.*, 1916, **22**, 58; 1918, **24**, 335; *Zeitsch. physikal. Chem.*, 1913, **85**, 351; 1923, **106**, 426; *Ber.*, 1923, **56**, 696.

[5] See *Treatise on Physical Chemistry*, chap. xviii. p. 1226 (D. van Nostrand Co., New York, 1924; Macmillan & Co., London, 1925).

between light energy absorbed and chemical energy produced. It would be difficult to devise analogous chain systems to the above for the reactions between carbon monoxide and chlorine, methane and chlorine, xylene and bromine, in all of which, however, marked deviations from the law of the photochemical equivalent occur and which also show great sensitivity to the presence of inhibitors. The existence of such deviations from photo-equivalence demands, however, some mechanism of reaction whereby initial photo-process is succeeded by a very large number of spontaneous processes, the activating energy for which must come from the reaction energy produced in the processes set in motion by the original photo-reaction. The nature of the energy transfer involved and the steps by which it is achieved are, at the moment, quite unexplained. The problem involved forms a most important phase of our study of the mechanism of chemical change. It is more important and more complex by reason of the fact that such a succession of reactions can be disturbed or diminished by the presence of small quantities of inhibitors. In the succeeding paragraphs examples will be multiplied of reactions which involve some type of chain mechanism and show also the phenomenon of inhibition.

In the case of the hydrogen-chlorine combination it is known that the nitrogen-containing organic inhibitors are consumed in the course of the reaction. Their effect, therefore, progressively decreases as the reaction proceeds, and it is to the presence of such bodies that the well-known phenomenon of the induction period in photo-halogenations is to be ascribed.[1] As regards the function of oxygen in the inhibition of the hydrogen-chlorine combination, Weigert [2] and more recently Rideal and Norrish [3] have shown that chlorine sensitises the reaction between hydrogen and oxygen to visible light, and that oxygen is removed from the reaction mixture as water vapour. The reaction velocity is proportional to both the chlorine and the oxygen concentration, so that it seems that the excited chlorine molecule transfers its energy by collision to an oxygen molecule, rendering it reactive thereby. With regard to the traces of oxygen normally present in the mixtures used in the studies of the hydrogen-chlorine combination, no special experiments have been made to ascertain what products result from their presence nor the mechanism of their inhibitory action. Bodenstein [4] assumed that the oxygen was, in some manner, maintained at constant concentration throughout the reaction. This point requires further study in view of the above study with higher concentrations of oxygen. The presence of oxygen, however, even in small concentrations, decreases the length of the chain reactions initiated by the absorbed light, and, as far as present data show, to an extent proportional to its concentration in the hydrogen-chlorine mixture.

[1] Chapman and co-workers, *J. Chem. Soc.*, 1906, **89**, 1402; 1909, **97**, 845. See also, however, Baly and Barker, *J. Chem. Soc.*, 1921, **119**, 653.

[2] *Ann. Physik*, 1907 (4), **24**, 55, 243.

[3] *J. Chem. Soc.*, 1925, **127**, 787.

[4] *Zeitsch. physikal. Chem.*, 1924, **114**, 208.

A further insight into the mechanism by which chain reactions are stopped by inhibitors present in small concentrations has been gained by the investigations of Weigert, Coehn and Jung, and Norrish (see *ante*, p. 151) on the hydrogen-chlorine reaction. The hydrogen-chlorine mixture is only sensitive to visible light in the presence of minute amounts of water vapour. The experiments of Norrish indicate that the photo-sensitive reactant is a chlorine water complex; this complex when excited by absorption of radiation is chemically reactive in starting chains. This may be due either to an enhanced stability or life of an excited chlorine molecule or to the direct formation of hydrogen chloride according to the reaction $Cl_2H_2O + H_2 \longrightarrow 2HCl + H_2O$. Further experiments are required to elucidate this point. In the presence of inhibitors such as ammonia the free water is removed, and on excitation of the remaining chlorine reaction with ammonia takes place; thus inhibition results by stopping the chains from commencing, not from breaking a chain which has already been started.

The inhibition of hydrogen-peroxide decomposition. — The decomposition which solutions of hydrogen peroxide undergo both thermally and photochemically can be inhibited by suitable additions of selected substances. Acids of all kinds, salts such as sodium and calcium chlorides, sodium pyrophosphate, magnesium silicate, alcohols, glycerol, ether, esters, naphthalene, amines, phenols, acetanilide, are typical agents of inhibition.[1] The last-named substance has found a considerable technical application for this purpose and possesses a dual efficiency both for the thermal and the photochemical decomposition. This dual efficiency is not always obtained. The presence of alkalis markedly accelerates the thermal decomposition and inhibits the photochemical decomposition, a factor which is not yet satisfactorily explained.

The photochemical studies of the decomposition process have provided the experimental indication that the reaction in question has some type of chain mechanism. Henri and Wurmser[2] showed that the light absorption was weak, and that as many as 100 molecules of the peroxide are decomposed for every quantum of light energy absorbed. This conclusion has been verified by Kornfeld[3] using monochromatic illumination and exact methods of energy absorption measurements. Her results show that the actual number of molecules decomposed per unit of energy absorbed increases with increasing concentration. In solutions 0·016 normal with respect to peroxide, twenty-four molecules decomposed per quantum. In 0·05 normal

[1] For a summary of the photochemical literature see Anderson and Taylor, *J. Amer. Chem. Soc.*, 1924, **45**, 650, 1210. For the literature of the thermal decomposition see Davis, *Chem. News*, 1884, **49**, 226; Sabatier, *Bull. Soc. chim.* (2), 1885, **44**, 169; Kingzett, *J. Soc. Chem. Ind.*, 1890, **9**, 3; *J. Soc. Chem. Ind.*, 1906, **25**, 1219; 1908, **27**, 1214; 1909, **28**, 1314; 1910, **29**, 159; *Bull. Soc. Ind. Mulhouse*, 1895, 78; 1897, 95; Clayton, *Trans. Farad. Soc.*, 1916, **11**, 164.

[2] *Compt. rend.*, 1913, **156**, 1012.

[3] *Zeitsch. wiss. Phot.*, 1921, **21**, 66.

solutions, the number had risen to seventy-seven molecules. Evidently the chain mechanism becomes more efficient in the more concentrated solutions, or what is the same thing, solvent water molecules break the chains. In acid solutions of the peroxide, the number of molecules decomposed per unit of energy absorbed is markedly lowered. Henri and Wurmser [1] listed a number of inorganic compounds which inhibit the light reaction, and in the following year Mathews and Curtis [2] added a number of organic and inorganic compounds. They failed to observe any properties possessed in common by the inhibitors. Recent investigations by Anderson and Taylor [3] have tended to elucidate the mechanism of certain of these inhibitions. The inhibitory effects exhibited by typical organic compounds of known absorption spectra were examined in four definite spectral regions of the ultra-violet. The inhibition by such agents was associated with the absorption capacity of the compounds for ultra-violet light. A striking correlation between these two factors was obtained in the case of benzene, several esters, acids, amides, ketones, and alkaloids. The inhibitors act more efficiently when in the peroxide solution than when in a screening solution of similar thickness and concentration. This is doubtless to be associated with the existence of the chain reactions already mentioned. These inhibitors act therefore in a twofold capacity. They absorb some of the radiation which might activate hydrogen peroxide molecules. They apparently, also, break whatever chain mechanism may be set up [4] to account for the abnormal photochemical yield. Not all inhibitors act in the former capacity. Certain aliphatic alcohols and amines, halogen, hydroxyl, and hydrogen ions act as inhibitors, although quite diactinic in the ultra-violet. Possibly adsorption of the inhibitor on the active portions of the reaction vessel, resulting in a decrease of the number of chains started, may be found to play an important part in the process.

Oxidation processes.—It has already been pointed out that in many processes of oxidation the inhibitor may act by removal of a powerful positive catalyst, the oxidation of sodium-sulphite solutions by dissolved oxygen being studied in detail by Titoff. The number of such autoxidation reactions sensitive to inhibitors has been largely increased by various investigations, among which some of the more important are due to Moureu and Dufraisse.[5] Their earliest work showed that the prevention of autoxidation of a variety of substances, for example benzaldehyde and acrolein, was possessed by phenolic compounds. The efficiency of such compounds was remarkable. One molecule of hydroquinine in every 40,000 molecules of acrolein served to make the autoxidation of the latter negligible. Analogous results

[1] *Compt. rend.*, 1913, **157**, 284. [2] *J. Physical Chem.*, 1914, **18**, 521.
[3] *J. Amer. Chem. Soc.*, 1923, **45**, 650, 1210.
[4] See Kornfeld, *loc. cit.*, and Nernst and Noddack, *Sitzungsber. preuss. Akad.*, 1923, 112.
[5] *Compt. rend.*, 1922, **174**, 258; 1922, **175**, 127; 1923, **176**, 624, 797; 1923, **178**, 824, 1498, 1861; 1924, **179**, 237.

were obtained with such autoxidisable substances as acetaldehyde, chloral, propionic aldehyde, anisic aldehyde, cinnamic aldehyde, hydrocinnamic aldehyde, furfurol, styrolene, turpentine, linseed oil, nut oil, and butter. Furthermore, various secondary phenomena which often accompany autoxidation processes generally related to molecular condensations and manifested by changes of colour, precipitates, change in viscosity, rancidity are also inhibited by such additions. Thus, furfurol, instead of turning deep black, remains almost colourless; acrolein no longer yields dis-acryl, a polymerised product; styrolene remains fluid; linseed oil can be exposed in thin layers without losing its fluidity; fatty bodies do not become rancid.

Further afield, Moureu and Dufraisse have noted the French patent to the Società Anonyma Co-operativa (1905), which claims the protection of silks against light, heat, and atmospheric action by means of thiourea, hydroquinine, and their derivatives, this patent being a product of the investigations of Sisley and Seyewetz;[1] also a German patent (1918) to the Badische Anilin- und Soda-Fabrik claiming the protection of synthetic rubber against autoxidation by the presence of phenolic compounds. Gillet and Giot[2] have noted that materials dyed with azo dyes and eosin dyes are protected against colour changes by such inhibitors as Moureu and Dufraisse have studied. Rubber oxidation is inhibited by tannin and hydroquinone.[3]

Moureu and Dufraisse reject the Titoff concept of suppression of a positive catalyst and have formulated a theory of mechanism which seeks the theoretical solution of the problem of autoxidation in the "peroxidation" of both autoxidant and inhibitor, followed by interaction of the two oxidised agents to regenerate both initial substances and elementary oxygen. Thus, if A be the autoxidisable substance and B be the inhibitor, the sequence of reactions would be

$$A + O_2 = A(O_2), \quad A(O_2) + B = A(O) + B(O),$$
$$A(O) + B(O) = A + B + O_2;$$

or alternatively,

$$A + O_2 = A(O)_2,$$
$$B + O_2 = B(O_2),$$
$$A(O_2) + B(O_2) = A + B + 2O_2.$$

The later papers of Moureu and Dufraisse have been concerned with data designed to prove this mechanism, inhibitors such as iodine and iodine compounds, compounds of sulphur and of phosphorus having been studied. They note that most inhibitors are easily oxidisable substances.

It has long been known[4] in connection with induced oxidation

[1] *Bull. Soc. chim.*, 1922, **31**, 672.
[2] *Compt. rend.*, 1923, **176**, 1402.
[3] *Compt. rend.*, 1923, **177**, 204. F.P. 509607/1919.
[4] See Chapter VII.

processes that, during many processes of autoxidation, for every molecule of oxygen consumed by the substance undergoing oxidation a molecule of oxygen was simultaneously activated and could react to form ozone, hydrogen peroxide, or in the presence of other autoxidisable substances could oxidise them, frequently causing oxidations which cannot be accomplished by ordinary atmospheric oxygen. One such case, studied by Jorissen,[1] is the oxidation of potassium arsenite, present in solutions of sodium sulphite undergoing oxidation. Oxidation of arsenite solutions by dissolved oxygen does not occur. In presence of sulphite, however, equimolecular quantities of the two oxidation products are obtained. In the induced reaction the oxidation of the sulphite is materially lower than in the absence of arsenite. The latter can therefore be regarded as an inhibitor of the sulphite oxidation. Jorissen suggests[2] that the oxidation of a sulphite-arsenite complex occurs. Moureu and Dufraisse have elaborated their theory[3] to explain these cases. Such special explanations cannot have general applicability since it is certain that in many cases oxidation of the inhibitor does not proceed at the same rate molecularly as that of the autoxidisable substance. Furthermore, it would be desirable even in the case of sulphite-arsenite mixtures to ascertain whether the relative amounts of the two oxidised does not vary with the concentrations present.

Reasoning from the existence of chain reactions in photochemical processes and from the form of the kinetic equation of a simple bimolecular reaction involving collisions, Christiansen[4] concluded that reactions sensitive to inhibitors, thermal as well as photochemical, might involve a chain mechanism. Reactions in which a minute amount of inhibitor effects a very considerable reduction in reaction velocity would, in such case, be those in which the length of the chain in absence of inhibitor is great, as in the hydrogen-chlorine photoreaction already discussed. There appears to be no ready method of ascertaining whether a purely thermal reaction has a chain mechanism. Photo-reactions, however, can readily be tested by a study of light energy input and chemical reaction which results. If a chain mechanism is established for a photo-reaction it is apparent that the processes succeeding the initial light absorption are not essentially different from thermal processes. If a photo-reaction is shown to have a chain mechanism, it is probable that the same reaction conducted thermally will also involve chains.

From this point of view Taylor[5] and also Bäckstrom[5] have investigated a number of oxidation processes photochemically to ascertain the ratio of light energy input to resultant chemical reaction. Bäckstrom studied both the oxidation of aldehydes such as benz-

[1] *Zeitsch. physikal. Chem.*, 1897, 23, 667. [2] See also *Rec. trav. chim.*, 1924, 43, 582.
[3] *Rec. trav. chim.*, 1924, 43, 645. [4] *J. Physical Chem.*, 1924, 28, 145.
[5] Unpublished experiments.

aldehyde and of sodium sulphite. He found in each case that many hundred molecules of the autoxidant react for each quantum of absorbed light energy. Mathews and Dewey [1] and Mathews and Weeks [2] showed that photochemical oxidation of sulphite was sensitive to inhibitors. Pyridine, benzaldehyde, phenol, hydroquinine, ethyl acetate, urea were all retarding agents of varying efficiency. There is, however, some divergence between the thermal and photochemical processes, since copper salts which are powerful catalysts for the thermal process are without action photochemically. The photochemical oxidation of benzaldehyde is retarded by many of the inhibitors of the thermal process. Taylor showed that in the photo-oxidation of an unsaturated glyceride a chain mechanism might also be involved, since the ratio of molecules reacting to quanta absorbed was greater than unity though much smaller than in the cases studied by Bäckstrom.

Young [3] showed that the oxidation of solutions of stannous chloride in water by dissolved oxygen was likewise extremely sensitive to the presence of inhibitory substances. Various alkaloids, mannite, aniline, potassium cyanide, salts of manganese and of chromium were shown to be inhibitors. It is not yet known whether this is an additional case of a reaction involving a chain mechanism. Young showed that it was sensitive to certain positive catalysts present in minute amounts. A concentration of 0·000005 N hydrogen sulphide serves to increase the rate of oxidation by about 25 per cent.

Gaseous oxidations. — Recent investigations have shown that certain gaseous oxidation processes are sensitive to the presence of inhibitory agents. This discovery arose in connection with a study of the explosion of hydrocarbon-air mixtures in the automobile engine. Midgeley [4] has shown that addition of agents, such as iodine, amines, and especially lead tetra-ethyl, to the motor fuel suppresses the tendency to pre-ignition of the explosive mixture in the cylinder, thereby permitting a higher compression to be employed. Corresponding economies in fuel consumption can thereby be secured.

There is no general agreement, as yet, with respect to the function of these added substances in hydrocarbon - air mixtures, various theories having been brought forward.[5] That such substances may act as inhibitors of oxidation was shown by Taylor by demonstrating [6] that lead tetra-ethyl is a powerful inhibitor of the autoxidation of benzaldehyde. On Christiansen's view the mechanism must be one involving a chain mechanism, the energy of the reaction products being transferred to the reactants bringing them into the reactive state, the inhibitor acting by breaking the chains. The view that the explosion reactions involve chains is in harmony with the conclusions

[1] *J. Physical Chem.*, 1913, **17**, 211.
[2] *J. Amer. Chem. Soc.*, 1917, **39**, 635.
[3] *J. Amer. Chem. Soc.*, 1901, **23**, 119, 450.
[4] *J. Ind. Eng. Chem.*, 1923, **15**, 421.
[5] *J. Ind. Eng. Chem.*, 1923, **15**, 421.
[6] A.C.S. Intersectional Meeting, Boston, 1924.

of Dixon [1] from his work on the explosion of combustible gas-air mixtures. It is of interest in this connection, also, to record that Humphry Davy [2] made experiments in 1817 on the influence of hydrogen chloride and silicon tetrafluoride on the lower explosion limit of hydrogen. He showed that a mixture of two volumes of hydrogen with one of oxygen did not explode when 2 per cent by volume of hydrogen chloride or 0·8 per cent of the silicon compound was added. Jorissen, Velisek, and Menwissen have recently studied [3] the restriction of the inflammability limits of explosive gas mixtures in presence of various chlorinated hydrocarbons. Further work is needed before the theoretical elucidation of this most important practical problem can be achieved. From such work it may be anticipated that the mechanism whereby the chains are broken will be elucidated. As yet, there is little information on the point. There is some evidence that the inhibitor is oxidised in processes of oxidation. It is also possible that the energy of a "hot" molecule may be dissipated by molecular compound formation with the inhibitor, since, as was shown by Taylor,[4] there is a marked concordance between inhibitory power and ability to form molecular compounds.

[1] *Ber.*, 1905, **38**, 2441.
[2] *Phil. Trans.*, 1817, 59.
[3] *Rec. trav. chim.*, 1924, **43**, 80, 591.
[4] *J. Physical Chem.*, 1923, **27**, 322.

CHAPTER VII

PROCESSES OF OXIDATION

THE most varied and extensive application of catalysis to the problems of industrial chemistry has been made in the technical development of processes of catalytic oxidation.

Catalysts have been successfully employed to accelerate various processes of oxidation extremely dissimilar in character. Thus, in processes of surface combustion the catalytic material induces the *complete* combustion of gaseous and vaporised fuels for the production of intense and localised heat, whilst, on the other hand, the incandescent mantle exhibits similar localised combustion for the production of light. In those cases also in which the process of oxidation is reversible within the usual temperature range of operation, as in the oxidation of sulphur dioxide to sulphuric anhydride or of hydrochloric acid to chlorine and water, technical development was only possible after the discovery of catalytic agents which would accelerate the processes of oxidation at relatively low temperatures so as to ensure the maximum yield of the desired product at reasonable space velocities.

Another extending field for the technical development of processes of catalytic oxidation is to be found in the cases of *fractional oxidation*, where, by the choice of suitable catalytic material and the proper conditions of temperature, pressure, and concentrations of reacting substances, the reaction is caused to proceed along one path only, with the avoidance of possible side reactions or products of combustion of a higher or lower state of oxidation than is desired. Mention may be made of the technical processes for the oxidation of ammonia to nitric oxide, of hydrogen sulphide to sulphur, of methyl alcohol to formaldehyde, and of naphthalene to phthalic anhydride as examples of such fractional oxidation. In all these cases, under adverse conditions, the yield of the desired product may be reduced to nil.

Processes of catalytic oxidation may also be *selective* in character. Thus, iron sulphide may be oxidised in the presence of the inflammable constituents of coal gas by the regulated admission of air under suitable temperature control. Mixtures of methane, hydrogen, and carbon

monoxide may be analysed by the admission of oxygen, the combustion being conducted in such a manner that, by a suitable choice of catalytic material and operating temperature, only one constituent undergoes oxidation.

The classical experiments of Schönbein on autoxidation, in which the reaction velocity of the process of oxidation is extremely slow, opened up a new and interesting chapter in the theory of combustion. The significance of such processes of cold combustion will at once be apparent from a consideration of the mechanism of the corrosion or rusting of metals and the many remarkable cases of induced chemical reactions which accompany processes of autoxidation.

In the following pages examples are given of the varied and manifold applications of catalysis to these diverse processes of oxidation. It will be noted that, as in many other cases, practice, as exemplified by technical development, has outstripped the theoretical treatment of the subject.

The Manufacture of Sulphuric Acid

The sulphuric acid industry is practically unique in the fact that the two processes employed on an ever extending scale for its manufacture, the so-called "chamber" and "contact" processes, are both catalytic in operation, and in the most modern plants the relative costs of production are practically identical. The "chamber" process, however, is confined to the production of the monohydrate, the maximum strength of acid obtainable being 98 per cent H_2SO_4, whereas the "contact" process is more suitable for the production of "oleum", *i.e.* sulphuric acid containing varying amounts of SO_3 dissolved in it, pure "oleum" or fuming acid having the composition $2SO_3 . H_2O$ or $H_2S_2O_7$.

The "chamber" process.—In this process the oxidation of sulphur dioxide to sulphuric anhydride by means of atmospheric oxygen is catalytically hastened by oxides of nitrogen, and is one of the very few cases of homogeneous catalysis in a gaseous system.

In actual operation a 6 to 12 per cent mixture of sulphur dioxide in air obtained by passing a regulated amount of air over burning sulphur or sulphides such as pyrites, or spent oxide from gas works, is brought into contact whilst still hot (400°) with a solution of nitrosyl sulphuric acid, by passage through one or two volvic lava- or flint-packed columns termed Glover towers, down which a stream of nitrosyl sulphuric acid is distributed.

The resulting mixture of sulphur dioxide, oxides of nitrogen, and air then pass into a series of leaden chambers into which steam or dilute sulphuric acid is blown by means of suitably shaped nozzles. The earlier rectangular reaction chambers, which would only produce one-sixth of a pound of sulphuric acid per cubic foot in twenty-four

hours, are now replaced either by tangential chambers in which nearly $1\frac{1}{2}$ lb. of sulphuric acid can be produced per cubic foot in the same time, or by plate or packed towers in which the oxidation of the sulphur dioxide to the trioxide no longer takes place in the gaseous phase, but in the dilute nitric acid which is added to each tower. Although a considerable economy in space is gained in such tower systems, yet the extra installation costs and the increased resistance to the gas passage bid fair to militate against this advantage.

The spent gases from the reaction chambers are freed of all residual oxides of nitrogen by passage up a coke or stoneware ball-packed column, the Gay-Lussac tower, down which sulphuric acid is distributed. The weak sulphuric acid from the lead chambers (*ca.* 65 per cent) containing both oxides of nitrogen and nitric acid mixed with the nitrous vitriol from the Gay-Lussac tower, is partially concentrated (to 78 per cent) in the Glover tower, where the oxides of nitrogen are removed by the fresh gases and finally brought up to 98 per cent strength by evaporation in Gaillard towers or by means of cascade concentrators.

It is evident that under ideal conditions the oxides of nitrogen which are continually returned to the reaction chambers by means of the Glover tower should suffer no diminution during the cycle of operations. In actual practice, however, there is a small but continuous loss of the catalyst equivalent to from 1 to 4 parts of sodium nitrate in 100 parts of sulphur burnt. This deficit has to be continuously made good either by the addition of nitric acid to the Glover tower or by supplying oxides of nitrogen to the entering gases. In the latter case either small quantities of sodium nitrate (nitre) and sulphuric acid are placed in pots situated in the flue of the pyrites burners, or in the most modern practice, oxides of nitrogen, produced by the catalytic combustion of ammonia (see p. 165), are added at the base of the Glover tower.

The loss of oxides of nitrogen in the cycle is probably due to a variety of causes, amongst the more important of which may be mentioned:

(*a*) The presence of organic matter in the sulphur dioxide—a common occurrence when spent oxide is utilised.

(*b*) Loss in the sulphuric acid finally produced and at the exit of the Gay-Lussac tower.

(*c*) The reduction of nitric oxide to nitrous oxide or nitrogen by the coke packing in the Gay-Lussac tower, and by decomposition in those parts of the contact chambers where the acid is under 40 per cent strength.

An explanation of the mechanism by which the oxidation of sulphur dioxide to the trioxide is accomplished with the aid of oxides of nitrogen was first suggested by Davy in 1812, as a result of a series of experiments which had been conducted some six years previously by Clément

and Désormes.[1] It was noted that when insufficient steam was admitted to the reaction chambers white crystals of nitrosulphonic acid were deposited; Davy's hypothesis for the oxidation was based upon the intermediary formation of this acid, according to the following equation:

$$(1)\quad 2SO_2 + H_2O + 3NO_2 = 2SO_2\begin{<}OH\\NO_2\end{>} + NO,$$

the nitrosulphonic acid reacting with excess of steam and oxygen to form sulphuric acid:

$$(2)\quad 4SO_2\begin{<}OH\\NO_2\end{>} + 2H_2O + O_2 = 4SO_2\begin{<}OH\\OH\end{>} + 4NO,$$

whilst the nitric oxide is reoxidised to nitrogen dioxide as follows:

$$(3)\quad 2NO + O_2 = 2NO_2.$$

Lunge and Naef in 1884 found, on analysis of the chamber gases in the second and third chambers, that nitric oxide and nitrogen dioxide were present in equivalent proportions, behaving as N_2O_3:

$$(4)\quad NO_2 + NO \rightleftarrows N_2O_3,$$

and suggested the following series of reactions to account for the formation and subsequent decomposition of chamber crystals:

$$(5)\quad 2SO_2 + O_2 + H_2O + N_2O_3 = 2SO_2\begin{<}OH\\NO_2\end{>},$$

$$(6)\quad 2SO_2\begin{<}OH\\NO_2\end{>} + H_2O = 2H_2SO_4 + N_2O_3.$$

In the first chamber the gases are usually colourless owing to a deficiency of nitrogen dioxide. Lunge and Naef suggested that the removal of this constituent was taking place by means of a side reaction, as follows:

$$(7)\quad 2SO_2\begin{<}OH\\NO_2\end{>} + 2H_2O + SO_2 = 3SO_2\begin{<}OH\\OH\end{>} + 2NO,$$

which would thus explain the presence of the nitric oxide in excess of the equivalent proportions demanded by Equation (4). These comparatively simple reactions, according to Raschig[2] and Trautz,[3] are not a sufficient explanation for all the phenomena observed when sulphurous

[1] See Lunge, vol. i.; Raschig, *J. Soc. Chem. Ind.*, 1907, **10**, 965; 1911, **30**, 106; Partington, *The Alkali Industry*, 1918.

[2] *Annalen*, 1887, **241**, 200.

[3] *Zeitsch. physikal. Chem.*, 1888, **2**, 608.

or sulphuric acids are agitated with oxides of nitrogen. It is common knowledge that in the usual nitrometer estimations a purple or pink coloration is nearly always present towards the end of the reaction.

The composition of the purple acid is unknown, but in all probability contains the nitroso-group, NO, to which its colour may be attributed.

Trautz postulates the formation of an unstable nitrosulphonic acid according to the following reactions :

$$2SO_2\begin{matrix}OH\\H\end{matrix} + N_2O_3 = 2SO_2\begin{matrix}OH\\NO\end{matrix} + H_2O,$$

$$2SO_2\begin{matrix}OH\\NO\end{matrix} \longrightarrow SO_2\begin{matrix}OH\\NO\end{matrix} + NO,$$
$$SO_2\begin{matrix}\\OH\end{matrix}$$

which is subsequently decomposed according to the following two side reactions :

(1) $$SO_2\begin{matrix}OH\\NO\\OH\end{matrix} + N_2O_3 \longrightarrow 3NO + 2H_2SO_4,$$
$$SO_2\begin{matrix}\\OH\end{matrix} + H_2O$$

(2) $$SO_2\begin{matrix}OH\\NO\\OH\end{matrix} + 2SO_2\begin{matrix}OH\\NO_2\end{matrix} + 2H_2O = 4H_2SO_4 + 3NO.$$

The existence of a hypothetical nitrosulphuric acid $SO_2\begin{matrix}OH\\O\,.\,NO_2\end{matrix}$ has also been suggested by Lunge, formed by the interaction of nitric acid vapour on sulphur dioxide in the presence of air :

$$O_2 + 2SO_2 + 2HNO_3 = 2SO_2\begin{matrix}OH\\O\,.\,NO_2\end{matrix}$$

It must, however, be admitted that our knowledge of the various side reactions which may occur between the oxides of nitrogen catalysts and the oxides of sulphur is far from complete, but it appears probable that the explanation advanced by Lunge and Naef represents the most important sequence of actions taking place under the conditions in actual chamber practice.

The "contact" process.—The early development of the lead

chamber process for the manufacture of sulphuric acid took place in the years 1740 and 1750.

In 1812 Davy, who was the first to point out the true function of the oxide of nitrogen in the oxidation of sulphur dioxide, suggested the possibility of using platinum sponge as a catalyst for the same purpose. Phillips, in 1831, may claim to have been the pioneer in testing Davy's suggestion on the industrial scale, but owing to the rapidity with which his catalytic material became poisoned the process was abandoned until 1875, when Squire and Messel succeeded in making the process a technical success for the production of "oleum". These investigators utilised pure gases obtained by the decomposition of sulphuric acid on hot brick surfaces or by the combustion of sulphur, the sulphur dioxide being subsequently purified by washing with water under pressure.

The rapid development in the contact process during the opening years of the present century is chiefly due to the work of Kneitsch and Krauss,[1] who carried out a very systematic investigation on the reaction velocities and the conditions of equilibrium of the reaction

$$2SO_2 + O_2 \rightleftarrows 2SO_3,$$

which was found by C. Winckler to be a reversible one. It was shown that the value of the equilibrium constant

$$K_p = \frac{P_{SO_3}}{P_{SO_2}\sqrt{P_{O_2}}},$$

where P_{SO_3}, P_{SO_2}, and P_{O_2} are the respective partial pressures of the reacting constituents, decreased with rising temperatures, as is observed from the following figures:

Temperature.	K_p.	Temperature.	K_p.
430°	198·0	600°	14·9
450	187·7	610	10·5
500	72·3	627	5·5
528	31·3	700	4·8
553	24·1	727	1·8

By means of the general equation

$$\frac{d \log K_v}{dT} = -\frac{Q_v}{RT^2},$$

assuming that the value of Q_v, the heat of reaction, which according to Berthelot and Bodenstein[2] is equal to an evolution of 21,700 cals. at the ordinary temperature, does not change seriously in value over the temperature range, we can calculate the value of K_v, and hence that of K_p, for any desired temperature. The value of the integration constant can be obtained by taking an experimentally found value of K_p or by means of Nernst's heat theorem.

[1] *Ber.*, 1901, **34**, 4069.

[2] Bodenstein and Finck, *Zeitsch. physikal. Chem.*, 1907, **60**, 1, 46.

The fractional conversion, *i.e.* the values of the ratio $\frac{SO_3}{SO_2+SO_3}=x$, could consequently be calculated when the magnitude of K_p had been determined. It is easy to show that the percentage conversion $100\,x$ is equal to

$$100\sqrt{P_{O_2}}\,\frac{K_p}{1+K_p\sqrt{P_{O_2}}}.$$

From this equation it is a comparatively simple matter to calculate the composition of the gas as it comes from the contact material in which equilibrium has been established, whilst the calculation of the final composition from an analysis of the entering gases can be made by means of the following equation :

$$100\,x=100\,\frac{K_p}{K_p+\dfrac{1}{\sqrt{\dfrac{b-0{\cdot}5\,ax}{100-0{\cdot}5\,ax}}}},$$

where a and b are the percentages of sulphur dioxide and oxygen in the initial mixture.

From these equations the following interesting facts can be deduced: first, that the ideal catalyst should be active at low temperatures, preferably below 500°, where the values of K_p are large; secondly, although an increase in the partial pressure of oxygen is beneficial in that it tends to raise the value of x nearer to unity, yet a limit is set to the quantity of air admitted by the effect of the diluent nitrogen. If we assume a mere trace of sulphur dioxide to be present in entering gases, *i.e.* a is approximately zero and $b=20{\cdot}9$ per cent, then

$$\sqrt{\frac{b-0{\cdot}5\,ax}{100-0{\cdot}5\,ax}}=\sqrt{\frac{b}{100}}=0{\cdot}457,$$

i.e.

$$100\,x=100\,\frac{K_p}{K_p+2{\cdot}2}.$$

For large values of K_p the yield is practically theoretical, but at 700° the value of $100\,x$ has sunk to 60 in spite of the very large quantities of oxygen present, whereas if no nitrogen had been present at all the value of $100\,x$ approximates to $\frac{100\,K_p}{K_p+1}$, or 83 at 700°. The optimum results are obtained when the quantity of excess air admitted to the pyrites burners raises the oxygen content to the ratio $SO_2 : O_2 :: 2 : 3$, or three times the theoretical amount for complete conversion to the trioxide.

Having determined the conditions governing the oxidation of the sulphur dioxide, Kneitsch and Krauss investigated the reaction velocity in the presence of different catalytic materials. Utilising purified

technical converter gas of the following composition: 7 per cent SO_2, 10 per cent O_2, and 83 per cent N_2, the speed of conversion was determined when passed over various catalysts at different speeds and varying temperatures. In Fig. 8 (Curves I and II) are shown the results of passing such a gas mixture over platinised asbestos in a porcelain tube at varying temperatures; it will be noticed that conversion with this, the most efficient of all the catalysts yet investigated, commences at 200° with a flow rate of 300 c.c. per minute (Curve I) and at a little under 300° with a flow rate of 20,000 c.c. per minute (Curve II), and as the flow rate increases a higher reaction velocity is required, necessitating a higher temperature with a correspond-

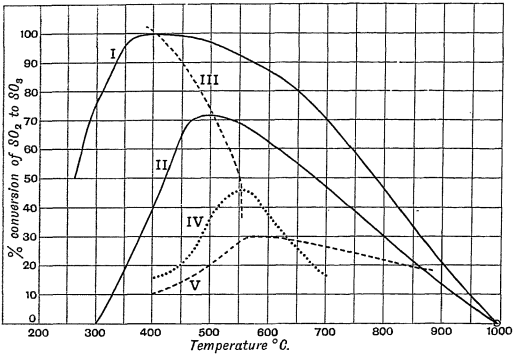


FIG. 8.

ing reduction in the equilibrium concentration of sulphuric anhydride obtainable. Curve III indicates the loci of the maxima of a set of the curves, utilising identical catalytic material, platinised asbestos and converter gas of similar composition but with different rates of passage.

It is evident that if some circulating system were employed, or alternatively a series of catalytic tubes were so arranged that the sulphur trioxide formed was removed after each catalytic treatment, the maximum conversion per unit of time would not be obtained with an operating temperature and speed of passage corresponding with the probable maximum conversion, but would entail a very high rate of passage with a relatively low conversion, the speed and temperature being so adjusted as to ensure the product, per cent conversion × flow

rate being a maximum. Technical difficulties associated with the removal of the sulphur trioxide from a gas containing relatively large quantities of the lower oxide appear to have prevented the realisation of this possible procedure.

Curve IV indicates the results obtained with burnt pyrites (CuO,Fe_2O_3) as contact material with a flow rate of 500 c.c. per minute, whilst Curve V shows the low duty obtained with broken porcelain as catalytic agent.

We have already referred to the employment of purified converter gas by several investigators. Squire and Messel appear to be the first to have realised the significance of catalyst "poisons" in the ordinary gas, and used, as an alternative, sulphur dioxide prepared from some purer source. The Badische Anilin- und Soda-Fabrik successfully solved the technical problem of purifying ordinary converter gas from poisons, notably arsenic, antimony, phosphorus, and lead, by steam treatment, cooling, and washing. The resulting gas is so purified as to be optically pure, showing complete freedom from suspended matter even when subjected to intense illumination.

Since the optimum conversion temperature lies between 400° and 450°, it was evident that for the successful technical development of the process the entering gases should strike the catalyst at a temperature approximating as nearly as possible to this, and should leave the catalyst at sensibly the same temperature. The reaction, however, is strongly exothermic, 21,700 cals. being evolved per grm.-mol. of sulphur dioxide converted. The Badische converter was accordingly constructed of relatively narrow iron reaction tubes, 10 per cent platinised asbestos being employed as catalytic material. The maximum radiation was thus obtainable by this method. A part of the inflowing gas, passing externally over the tubes in a counter-current direction, was so adjusted as to regulate the catalyst temperature, and at the same time assisted in heating up the remainder of the entering gases.

In the Mannheim process developed by Clemm and Hasenbach a preliminary conversion is effected by passage of the gases over burnt pyrites at from 500° to 600° where some 45 per cent conversion is effected. The gases freed from the sulphuric anhydride by absorption in strong sulphuric acid are then passed on to the lower temperature platinum catalyst. A dual advantage is thus obtained. In spite of the lower duty obtained with the burnt pyrites catalytic material on account of the somewhat elevated reacting temperature, this catalyst is not so sensitive to traces of poisons as the platinum and is a comparatively cheap material to utilise. As a further consequence, a very pure gas passes on to the platinum converter, and since nearly half of the sulphur dioxide has already been removed, the temperature of this catalyst can be easily adjusted within the prescribed limits.

Of the various catalytic materials employed to accelerate the

oxidation of sulphur dioxide to sulphuric anhydride, platinum is undoubtedly the most active, and much ingenuity has been displayed in obtaining the maximum yield possible with the aid of relatively small quantities of this somewhat expensive material.

In the Badische type of plant where platinised asbestos is utilised, the platinum is frequently deposited from the platinic chloride by means of a formate solution according to the method originally suggested by Loew.[1]

The Tenteleff process utilises a series of coarse asbestos string mats some 2 feet by 3 feet in area, impregnated with platinum black, from twelve to twenty-five being used as the contact mass; the quantity of platinum distributed on each mat varies from 60 to 65 grms.

The Schröder-Grillo contact material[2] is undoubtedly the most ingenious of any which are in operation, producing a very active form of platinum black and at the same time exposing a large area of catalytic surface.

Partially calcined magnesium sulphate is sprayed with a solution of platinum salt and heated up in the presence of sulphur dioxide, the reduction of the platinum being thus effected. From 0·2 to 0·3 per cent of platinum on the magnesium sulphate is sufficient to form an excellent contact material. With 5 grms. of platinum one ton of "oleum" can be produced per day with a loss of only 20 mg. of metal.

Of the various other catalytic materials suggested, it seems that only burnt pyrites has actually been used on an industrial scale. By reference to the patent literature, the problem of finding some other non-platinum catalyst more active than burnt pyrites is still the object of investigation. Amongst the more important materials suggested may be mentioned the oxides of copper, vanadium, uranium, chromium, nickel, and cobalt, frequently incorporated with aluminium, beryllium, zirconium, or zinc oxides, or the rare earths, such as didymia or ceria; thus vanadium pentoxide when precipitated in a fine state of subdivision on silica is stated to be as effective as platinum.[3] It is of interest to note that oxide of arsenic itself, although a poison for platinum, is a comparatively good catalyst at somewhat higher temperatures.[4] Water, on the other hand, inhibits the reaction very strongly by selective adsorption even up to 700° C. More novel is the suggestion to incorporate with the catalytic material some body which readily absorbs sulphur trioxide at the temperature employed, and disengages it again at a higher temperature.

Various theories have been put forward to explain the mechanism of the contact process; it is usually assumed that the intermediary formation of the platinum oxide, PtO, or the more transitory and possibly hypothetical dioxide, PtO_2, suggested by Wöhler and Engler,

[1] *Ber.*, 1890, **23**, 289. [2] *J. Soc. Chem. Ind.*, 1903, 22, 348. [3] G.P. 291792 of 1913.
[4] Lunge and Reinhart, *Zeitsch. angew. Chem.*, 1904, 1014; Koeppler, *ibid.*, 1908, 532.

plays the important rôle in this catalytic operation, according to the following cycle:

$$\text{(i.)}\quad 2Pt + O_2 \longrightarrow 2PtO + 2SO_2 \longrightarrow 2Pt\,.\,2SO_3.$$
$$\text{(ii.)}\quad Pt + O_2 \longrightarrow PtO_2 + 2SO_2 \longrightarrow Pt\,.\,2SO_3.$$

Wieland, however, has laid stress on the "hydration" theory of chemical action. Since perfectly dry sulphur dioxide and oxygen do not combine, he represents the oxidation of the sulphur dioxide as subsequent to a previous hydroxylation:

$$SO_2 + H_2O \longrightarrow H_2SO_3,$$
$$H_2SO_3 \longrightarrow SO_3 + H_2,$$
$$2H_2 + O_2 \longrightarrow 2H_2O.$$

It may be urged in favour of this view that in those cases where intermediate products of oxidation can be isolated and analysed—especially in organic reactions where the hydroxyl groups can be fixed and characterised as soon as they are formed by the substitution of a suitable non-reactive grouping—the evidence for hydroxylation as a stage in oxidation is remarkably strong.

It is extremely probable that adsorption phenomena exert a by no means inconsiderable influence on the rate of the reaction.

With oxide catalysts such as oxide of iron it is generally assumed that the formation of an intermediary sulphate occurs according to the following cycle:

$$\left.\begin{array}{l} 2Fe_2O_3 + 6SO_2 + 3O_2 \longrightarrow 2Fe(SO_4)_3. \\ 2Fe_2O_3 + 6SO_3 \longleftarrow \end{array}\right)$$

It is evident, however, by reference to the list of oxides suggested as suitable for technical processes, that practically only those elements are included which possess at least two oxides, and, as in many other catalytic processes, we are equally justified in assuming the catalytic activity to be due to an oscillation between the two states of oxidation:

$$Fe_2O_3 + SO_2 \longrightarrow 2FeO + SO_3$$
$$\uparrow \qquad\qquad \downarrow + O_2$$
$$\text{——————} Fe_2O_3,$$

$$CeO_2 + SO_2 \longrightarrow CeO + SO_3$$
$$\uparrow \qquad\qquad \downarrow O_2$$
$$\text{——————} CeO_2.$$

It must also be admitted that the explanation formed on the "intermediary sulphate" theory is not very satisfactory in the light of the researches of Bodenstein and Suzuki,[1] who showed that the first products of the distillation of ferric sulphate are SO_2 and O_2, which then react

[1] *Zeitsch. Elektrochem.*, 1910, **16**, 912.

in the presence of ferric oxide to produce SO_3, whereas SO_3 should be the primary product on this hypothesis.

Use of catalysts in the Hargreaves process.—Hargreaves and Robinson in 1870 introduced a method for the manufacture of salt cake (Na_2SO_4) by the interaction of pyrites burner gas and air on hot salt at 525°.

Above 600° fusion of the salt occurs, thus setting a limit to the temperature for the reaction. To accelerate the reaction at low temperatures, various catalysts have been proposed, notably ferric oxide [1] and copper oxide.[2]

It was suggested that the salt should be moistened with a solution of the sulphate of the metal so as to obtain an activated salt containing from 0·1 to 1·0 per cent of the metal.

The experimental investigation of the influence of copper and iron salts was reported by Conroy.[3] The conclusions reached are thus summarised. Salt is decomposed by a mixture of sulphur dioxide and air at a temperature below 600° to yield sulphate and chlorine. Decomposition in glass vessels is exceedingly slow. With addition of 0·25 per cent of copper in the form of sulphate, reaction begins at 400° and increases in amount with temperature.

The rate of action at 600° was roughly 50 per cent greater than at 450°. Increased concentration of copper increased the rate of reaction. It was shown that 0·5 per cent of iron as sulphate was catalytically equivalent to 0·25 per cent of copper. Magnesium and aluminium sulphates were without action. With suitable gas speed, reaction was quantitative, all sulphur dioxide being retained. At higher speeds of passage, both chlorine and sulphur dioxide escaped. The conversion to sulphate could be carried to completion.

In Conroy's view, the salts of copper and iron probably act by inducing the combination of sulphur and oxygen to form sulphuric anhydride, since, by inserting platinised asbestos in the inlet end of the reaction tube the ratio of the chemical equivalents of chlorine to sulphur dioxide and sulphur trioxide rose from 1 : 14 to 1 : 1. This method of working the process, viz. by passing a mixture of sulphur dioxide and air through vessels containing alternately a contact substance to produce sulphuric anhydride and salt, was patented by Deacon in 1871.[4]

To check fusion, Clemm proposed [5] to admix clay with the salt, utilising copper oxide or ferric oxide to aid the reaction.

The Oxidation of Ammonia to Nitric Acid

After the war the national interests, the increasing demand for nitric acid for growing industries in the various branches of organic

[1] Hargreaves, 1886.
[2] Kruhing and Dernoncourt, 1897; Clemm, 1899; and Hargreaves, 1907.
[3] *J. Soc. Chem. Ind.*, 1902, 21, 304. [4] B.P. 1908/1871. [5] B.P. 15152/1899.

chemistry and as nitrates for fertilisers, as well as the rapid strides recently made in the economic production of ammonia both as a coal by-product and in the form of cyanamide and pure ammonia manufactured by the various synthetic processes, have all tended to make the technical operation of an ammonia oxidation plant not merely a war industry but an integral part of the economic development of the State.

The pioneer work on this problem was accomplished by the French industrial chemist, Kuhlmann, in 1839, but until Ostwald and Brauer published their researches in 1903 no progress was made in the technical development of the process.

During the last few years several systems have been developed on an industrial scale, yielding on an average an efficiency of conversion of from 90 to 95 per cent. Amongst the more important may be mentioned those of Ostwald and Brauer, Frank and Caro, and that of Kaiser. Modifications and improvements of these German processes have been developed by the Allied Government Research Departments and by private firms during the period of the war, effecting a combination of the best features of the respective plants.

The oxidation of ammonia is effected by the passage of an air-ammonia or oxygen-ammonia mixture over a catalytic material maintained at a suitable temperature.

The oxidation may take place in two ways: the reaction of decomposition,

$$4NH_3 + 3O_2 = 2N_2 + 6H_2O + 301{,}000 \text{ cals.},$$

and the reaction catalytically accelerated,

$$4NH_3 + 5O_2 = 4NO + 6H_2O + 215{,}000 \text{ cals.}$$

Under the conditions of catalytic combustion the oxidation of ammonia is practically complete, as can be calculated from the Nernst heat theorem, assuming that the above equation is strictly reversible.

The heat liberated in the combustion of 4 molecules of ammonia under the above conditions is 215,000 cals. at 17°. For a homogeneous gas reaction we can calculate from Nernst's equation the equilibrium constant

$$K_p = \frac{p_{NH_3}^{\cdot} \times p_{O_2}^{\cdot}}{p_{NO}^{\cdot} \times p_{H_2O}^{\cdot}},$$

$$\log_e K_p = \frac{Q_0}{RT} + \frac{\Sigma\nu C_{0p}}{R} \cdot \log_e T + \frac{\Sigma\nu\beta}{R} + \Sigma\nu i,$$

where Q_0 and C_{0p} are the heat of reaction and the specific heats of the reactants at absolute zero, $\Sigma\nu$ the algebraic sum of the number of molecules, and i the integration constant of the vapour pressure formula.

For C_{0p} we can approximate the value 3·5 given by Nernst. The chemical constants for O_2, NH_3, NO, H_2O are 2·8, 3·3, 3·5, and 3·6

respectively, and $\Sigma\nu i = -8{\cdot}4$. Correcting the heat of combustion, viz. 215,000 for a temperature of absolute zero, taking into account the change in the specific heat of the gaseous constituents with the temperature, Q_0 will be found to be equal to 216,300 cals.

For temperatures of oxidation between 500° and 1000°, the range usually adopted in technical plants, or a mean of 800°, $C_p = C_{0p} + 2\beta T$.

$$2\beta = \frac{C_{p800^\circ} - 3{\cdot}5}{800}.$$

Hence $$\log_{10} K_p = \frac{216{,}300}{4{\cdot}57\,T} - 1{\cdot}75 \log T + \frac{0{\cdot}007}{4{\cdot}57} T - 8{\cdot}4.$$

For $\log K_p$ we find:

T.	$\log K_p$.
500°	− 108
800	− 71
1000	− 61

It will be observed that even at 1000° the quantity of ammonia in equilibrium with the nitric oxide under these conditions is almost vanishingly small and quantitative yields should always result.

In practice, quantitative yields are never obtained, for the following reasons:

(1) The time of contact of the air, or oxygen-ammonia mixture with the active surface of the catalyst may be too long. Under these conditions the nitric oxide formed by combustion with the ammonia will commence to dissociate and establish equilibrium, according to the equation

$$2NO \rightleftarrows N_2 + O_2.$$

This equilibrium is likewise governed by the temperature of the gas and is the basis of the arc process of fixing atmospheric nitrogen.

According to Nernst and Haber, the equilibrium amount of nitric oxide formed in air at 2000° is only 1·0 per cent varying to 10 per cent at 4140°, but is practically negligible at the working temperatures of the ammonia oxidation process (*circa* 0·001 per cent NO at 800°). On the other hand, the velocity with which equilibrium is established is greatly increased by a rise in temperature, and the gas containing the high concentration of the nitric oxide produced by combustion of ammonia must be rapidly cooled to decrease the velocity of the normal decomposition. It is evident from this consideration that the catalyst should be maintained at a low temperature and that the period of contact of the gases with the catalyst be as short as possible.

(2) Part of the ammonia may escape contact with the catalyst. Undecomposed ammonia present in the effluent gases will react with the nitrous acid formed on the condensation of the nitrogen oxides in water, with the liberation of nitrogen:

$$NH_3 + HNO_2 = N_2 + 2H_2O.$$

Twice the amount of nitrogen originally present in the escaping ammonia will thus be lost.

(3) Partial direct combustion to nitrogen may occur.

Ostwald and Brauer's process.—This system has been largely developed in Germany, whilst independent factories were established by the Nitrogen Products Co. at Vilvorde in Belgium, Angoulême in France, Dagenham in England, and at Legnano in Italy. As catalytic material, platinum foil is used in the form of a corrugated roll, about 2 cm. deep, 50 grms. in weight, loosely inserted in the end of a nickel tube some 2 metres long, and 9 cm. in diameter (solid drawn nickel is said to be preferable to welded tube). The nickel tube through which the ammonia and air mixture (*circa* 5 per cent NH_3) passes is enclosed by an enamelled iron tube somewhat wider in diameter, the whole system thus acting as a simple form of heat interchanger. The ammonia-air mixture is thus heated up to a temperature of 650° before striking the platinum roll, which is maintained at 650°-700° by the heat of combustion of the ammonia. The flowing gases, consisting of nitric oxide, nitrogen, and residual oxygen from the air, which is added in excess, are cooled down, and, after sufficient time of storage to ensure that the oxidation of the nitric oxide to nitrogen dioxide is complete, are passed into the nitric acid absorption towers.

Frank and Caro's process.—The disadvantages of the original process, namely, the lack of control of the catalyst temperature and the relatively large amount of platinum required to produce a given quantity of nitric acid (50 grms. will only produce some 30 tons per annum), led Frank and Caro to construct a form of converter in which a more economical utilisation of the catalyst (in this case platinum also was used) was attempted.

The converter of rolled aluminium consisted of a rectangular column containing baffle plates equally spaced and terminated by a conical hood of the same material. A fine platinum gauze (80 linear meshes to the inch of wire 0·0026 inch diameter) was stretched across the converter column, and by means of silver leads could be maintained at a uniform temperature (*circa* 650°) by the passage of an electric current. With the catalytic material in this form a somewhat richer air-ammonia mixture (9-11 per cent) could be dealt with and the converters constructed in considerably larger sizes. Technical units have been constructed up to 1 square foot in cross-section, whilst in America experiments on still larger units have been carried out. The output per square foot of catalyst surface is approximately 700 kilogrms. of nitric acid per 24 hours, whilst the weight of platinum is less than 40 grms. per square foot. The yield is stated to average 92 per cent.

Kaiser's process.—From 1911 to 1916 Dr. Kaiser, as a result of investigations carried out on a technical scale at Spandhau, near Berlin, put forward somewhat startling claims for a process developed by him.

In this process the single layer of platinum gauze is replaced by

four separated layers of similar material, the total thickness not exceeding 0·5 to 0·6 mm. Electrical heating is dispensed with, and the air previous to admixture with the ammonia is preheated by means of a coke fire to 300°-350°. Kaiser's original claims of efficiencies, exceeding 100 per cent owing to the simultaneous autoxidation of atmospheric nitrogen, have now been shown to be fallacious, and it appears possible that these were advanced only to overcome certain difficulties attached to the patent protection of his process.

The process was installed in a somewhat modified form by Saposhnikoff at Kharkoff in Russia, where an overall efficiency of over 92 per cent has been claimed. Recent experiments have also indicated that higher rates of gas flow and a consequent greater output per square foot of converter area are obtainable with multiple gauzes, although the actual output per grm. of platinum is somewhat lower. The average yield per square foot of converter area with two gauzes per 24 hours is 1·5 to 1·8 metric tons of nitric acid (in all cases calculated as 100 per cent).

Small plants using two or more gauzes are already installed in England for the supply of oxides of nitrogen in vitriol chambers and are giving 95 per cent yields continuously.

In modern plants preheating of the gas mixture is employed. It is found that the optimum temperature of the platinum gauze is *ca.* 1100 °C. Taking the mean specific heats of the products of oxidation as follows:

$$N_2 = 6{\cdot}88 \quad O_2 = 4{\cdot}00 \quad NO = 7{\cdot}50 \quad H_2O = 9{\cdot}20,$$

the heat content of a 1 : 11 NH_3 air mixture after combustion will be

$$\{8{\cdot}69N_2 + 1{\cdot}06O_2 + 1{\cdot}5H_2O + NO\}T = 85{\cdot}8\,T.$$

Hence, since the final temperature must be 1100° C., and since 54,000 cals. are evolved per grm.-mol. of ammonia burnt, we obtain

$$1100 - \frac{54{,}000}{85{\cdot}8} = 360°\ \text{C.}$$

as the optimum temperature of preheating.

A modern form of technical converter unit shown in the illustration (Fig. 9) is described by Partington[1] as follows: It consists of a top and bottom cone, with three rectangular body pieces between them, all in cast aluminium $\frac{1}{5}$ inch thick, the rectangular area exposed measuring 4 inches by 6 inches. The pieces are provided with flanges, $\frac{3}{4}$ inch wide, to facilitate bolting together, and three perforated baffles are inserted in all the junctions except that between the top cone and the top segment of the body, which is occupied by the catalyst frame. Though each cone possesses a sight orifice, $1\frac{1}{2}$ inch in diameter, for reasons of standardisation, that in the top cone alone is used, and is provided with a mica window for inspection of the catalyst. Aluminium bends of 2 inches internal bore provide inlets and outlets for the mixture

[1] *J. Soc. Chem. Ind.*, 1918, **37**, 337.

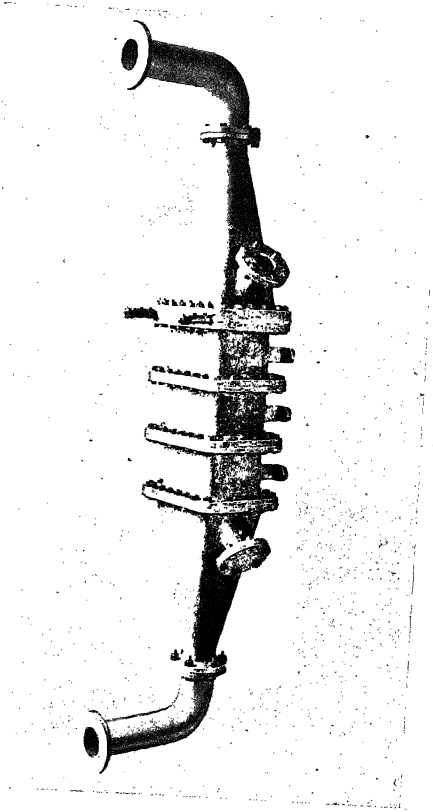


Fig. 9.

of air and ammonia at the bottom, and the oxides of nitrogen at the top, respectively. The overall length of the converter is about 4 feet and its weight is about 32 lbs.

The air supply is obtained from a blower, and it is essential that the air and ammonia should be well mixed. If ammonia gas is used, it may be injected into the air stream through a nozzle, after both gases have been measured. In technical practice it is more convenient to use purified ammonia liquor containing 25 per cent of ammonia, which is now a commercial article. The air is passed, together with a small amount of steam, into the base of a coke tower down which this liquor flows. The mixed gases are cooled in the upper portion of the tower, where the steam is condensed. The mixture of air and ammonia should be filtered, either by passage through a length of coke packing in the upper portion of the tower or through a filter packed with glass wool, which removes particles of dust. Oxide of iron particularly must be eliminated, as this has a deleterious effect on the platinum catalyst.

The most important part of the apparatus is the catalyst, which is fixed between the upper cone and body segment. It consists of one or more gauzes made of pure platinum wire, stretched across the converter at right angles to the gas flow. The wire used is 0·0025 inch in diameter, and is woven into gauze with 80 meshes to the inch. The gauzes are mounted in an aluminium frame. The reaction occurs during the very small interval of time in which the gases are in contact with the catalyst.

The operation of the catalyst must be initiated by heating the gauze, either by means of a non-luminous gas flame or by heating electrically with suitable current conducted through leads attached to the opposite edges of the gauze. When the first method is used, an orifice is provided in the upper body segment just below the gauze, which admits of the introduction of the flame, and is closed when the converter is in operation. The converter figured is provided with leads for electric current. When the reaction begins, the gauze is maintained at a red heat by the heat of oxidation, and the conversion proceeds uninterruptedly as long as the supply of air and ammonia is maintained. The platinum gauze may be used for about three months, after which it is desirable to replace it by a new gauze and to clean and refit. New gauzes are not very active at first, but acquire their full catalytic activity after a few hours' running.

The Catalysts employed in the Oxidation of Ammonia

Platinum.—It will be noted that all existing technical ammonia oxidation plants employ platinum [1] as a catalyst, and many interesting

[1] Recent information from Germany indicates that the use of non-platinum catalysts has been largely developed during the last two years.—E. K. R.

observations have been made as to the catalytic activity of platinum for this purpose. Kuhlmann, in 1839, first noted that platinum sponge was more efficient than platinum black for the production of oxides of nitrogen, but that larger yields of nitrogen were obtained with the latter. Bright platinum is scarcely active. Ostwald and Brauer [1] continued Kuhlmann's researches and showed that the optimum results were obtained when bright platinum was coated with an almost invisible film of grey or black platinum and that only a short period of contact was necessary, *i.e.* 0·01 second. Schick, in 1907, noted that platinised porcelain, of which the glaze was slightly fusible, permitting the coalescence of the platinum into minute droplets, was extremely active, and recent photomicrographic investigation of platinum gauze also indicates that there is a gradual increase in catalytic activity associated with the formation of minute craters on the metal, the lip of each crater being just tinged with "grey" or "black" platinum. By the use of such an active net the period of contact may be reduced to as low a figure as 0·0006 second. The illustrations (Fig. 10) given show the changes in structure of a gauze during use.

It seems probable that the black or grey platinum is the active catalyst, but when present in large quantities it is liable to cause the formation of nitrogen either in the primary oxidation of the ammonia, or, as seems more probable, due to secondary decomposition of the nitric oxide.

Poisons.—Small quantities of hydrogen sulphide rapidly poison the catalyst, but when the impure gases are replaced by purified ammonia-air mixtures a partial recovery of the poisoned catalyst always results. In the other cases of poisoning this process is, however, quite irreversible. As an example the following data for acetylene poisoning may be noted:

Time. Minutes.	Per cent yield.	Volume per cent Acetylene.
0	93·0	0
		Added 0·44
20	92·8	,,
26	91·4	,,
32	87·8	,,
38	72·3	,,
	Impurity removed.	
78	71·9	—
200	71·4	—

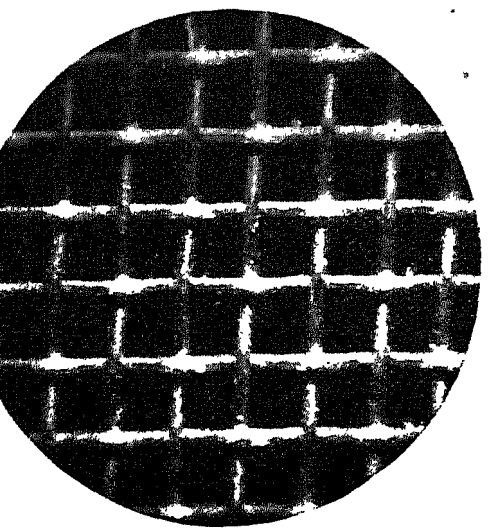
Whilst both hydrogen sulphide and acetylene are removed from the platinum surface and thus do not effect poisoning by covering the surface, they effect a partial fusion and crystallisation of the surface and thus diminish the catalytic activity.

Phosphine exerts a marked partially reversible poisoning action; a content of only 0·00002 per cent by volume will reduce the yield by no less than 20 per cent. On recovery a net yield of 80 per cent as compared with an original of 93 per cent can be obtained.

[1] *Chem. Zeit.*, 1903, **27**, 100.

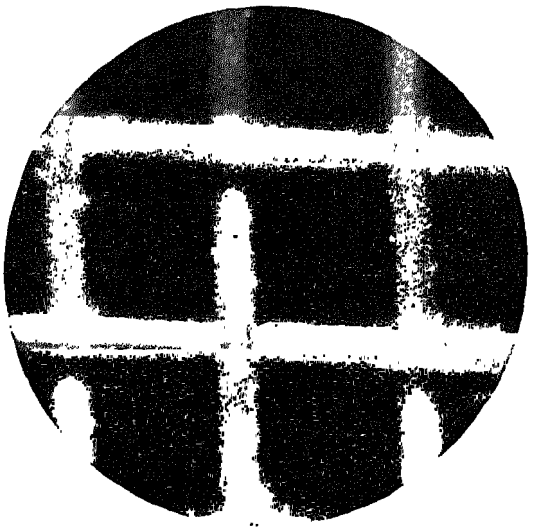
It is somewhat remarkable that hydrogen sulphide, which is feebly toxic in itself (1-2 per cent being required to exert a diminution of

PHOTOMICROGRAPHS OF PLATINUM GAUZE



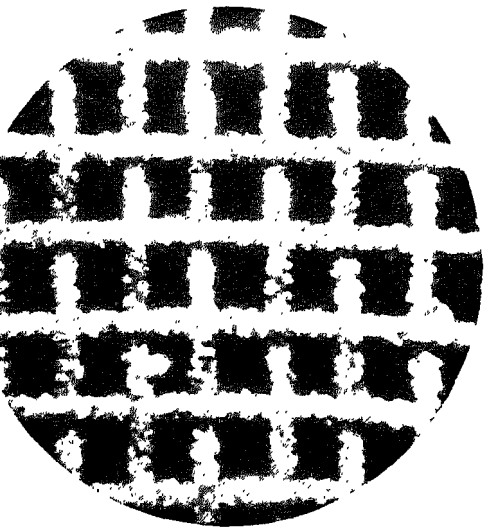
×24.

Plain wire before use.



×75.

Plain wire before use.



×24.

After some weeks' use.

×75.

After some weeks' use.

FIG. 10.

[*By permission of Messrs. Brunner Mond & Co., Ltd.*

10 per cent in the yield), exerts a curiously protective effect against the action of both acetylene and phosphine. Thus a mixture of gas con-

taining as impurity 0·38 per cent C_2H_2 and ·00002 per cent PH_3 will reduce the yield from 93 to 70 per cent in one hour. On the addition of 0·02 per cent of H_2S the yield commences to rise and will reach 86 per cent in less than two hours.

Non-volatile impurities, *e.g.* silica, ammonium phosphate, dust, oxide of iron, and the like, must naturally be rigorously excluded. Probably for this reason platinum impregnated on pumice or asbestos has a remarkably low efficiency.

Non-platinum catalysts.—Kuhlmann, in 1839, noted the catalytic activity of oxides of copper, iron, and nickel for this purpose, whilst Du Motay [1] proposed the use of alkaline manganates, permanganates, bichromates, and plumbites.

Ostwald and Brauer, in the series of researches previously alluded to, indicated the activity of the oxides of manganese, lead, silver, copper, chromium, nickel, cobalt, vanadium, and molybdenum, but stated that they were all inferior to platinum in catalytic activity. Frank and Caro [2] proposed the use of ceria and thoria, whilst Wendriner suggested the black oxide of uranium, U_3O_8.

During the period of the war, research in the utilisation of non-platinum catalysts has been extremely active, especially in America and Germany, where the dearth of platinum was somewhat acute. Although no non-platinum catalytic process has been assured of technical development,[3] nevertheless the results obtained on a small scale are sufficiently encouraging to justify their continuance.

Jones and Morton in the United States have reinvestigated Du Motay's alkaline plumbites, especially those of magnesium, zinc, cadmium, and aluminium, with success. Their reactivity towards metals and all forms of glass and silica at high temperatures is the chief objection to their use.

In England, Maxted [4] has investigated the use of oxides of iron admixed with certain promoters such as copper oxide, lime, or bismuth oxide. He has shown that the conversion of ammonia-oxygen mixtures can be accomplished in heated tubes, specially "activated" on the inside, with more than a 90 per cent efficiency. The short life of the catalyst under these conditions is the chief drawback to his process. The use of oxygen instead of air is obviously only permissible in conjunction with a synthetic ammonia plant in which the oxygen fraction from the liquid-air plant used in the preparation of the nitrogen would be available.

The Badische firm in Germany have investigated the effect of a great number of promoters on active or feebly active catalysts, such as tellurium and lead oxides on platinum, bismuth, chromium, and cerium oxides on iron oxide.

The yields under approximately identical conditions for a number of such mixed oxide catalysts are given in the following table:

[1] B.P. 491/1871.
[2] D.R.P. 234329.
[3] See *ante*, p. 170.
[4] *J. Soc. Chem. Ind.*, 1917, **36**, 777.

Mixed oxides of	Per cent yields.	Mixed oxides of	Per cent yields.
Fe	83·5	FeSb	82·5
FeBi	94·6	FeUr	82·0
FeCu	92·0	FePb	89·8
FeCe	90·0	FeMn	79·0
FeW	89·3	FeZn	67·0
FeTh	87·3	FeCa	64·0
FeK	83·0		

It will be at once evident that " oxygen carriers " appear to be the *ine qua non* for ammonia oxidation, and the enhanced activity of inary and ternary mixtures of the oxides of those elements which ossess at least two or more well-defined oxides indicates some relationhip in this case between the catalytic activity and the presence of an scillating higher and lower oxide functioning as an oxygen carrier. he presence of a number of oxides evidently increases the temperature ange of catalytic activity by affecting the stability of the oxides.

It is interesting to note that chromium oxide ex chromium salts is ractically inert, but the oxide obtained by the ignition of ammonium ichromate exerts a very marked catalytic activity.

The observation of Ostwald and Brauer, namely, that the period f contact with non-platinum catalysts must considerably exceed that ecessary for platinum, has been repeatedly confirmed. The practical ifficulties associated with the uniform heating, and at the same time nsuring a uniform stream-line flow through a shallow bed of small riquettes or powders of such materials, also presents grave technical isadvantages. These, however, seem to have been overcome in ertain German factories.

The Oxidation of Hydrochloric Acid

For the manufacture of bleaching powder, by the absorption of hlorine gas in slaked lime, large quantities of chlorine are annually onsumed, and consequently the economical production of chlorine ecomes one of the serious problems confronting the alkali industry in s course of development.

In 1823 the Leblanc soda process was introduced into England by uspratt. At first the hydrochloric acid resulting from the salt-cake rocess was turned into the air, but, owing to the pressure of the lkali Acts of 1863 and 1874, as well as the serious competition of the olvay ammonia-soda process introduced in 1866, the utilisation of ydrochloric acid in the most profitable manner became necessary to nsure the financial stability of the older Leblanc process. With the ncreasing extension of electrolytic methods for the production of soda om salt and the displacement of bleaching powder by liquid chlorine n the industries, it appears possible that the final development of these rocesses has now been reached.

The Deacon process.—The possibilities inherent in the oxidation of

hydrochloric acid by means of atmospheric oxygen attracted the attention of inventors at a very early date, notably Oxland in 1840, Vogel and Thibierge in 1855, and Binks in 1860. It was not, however, until 1868 that H. Deacon and F. Hurter established the process as a satisfactory technical industry.

In its earliest form the hydrochloric acid from the salt-cake pans

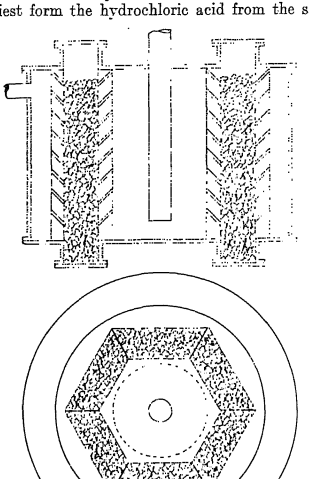


FIG. 11.

was mixed with four volumes of air and passed through iron superheaters to the contact chambers. The contact chambers or decomposing towers were iron cylinders about 12 feet wide filled with broken clay brick impregnated with cuprous chloride (Fig. 11) (the brick containing from 0·6 to 0·7 per cent of copper as the chloride), maintained at 500° by the waste heat from the superheaters. About two-thirds of the hydrochloric acid was found to be oxidised according to the equation

$$4HCl + O_2 = 2H_2O + 2Cl_2.$$

Condensation of the steam and unchanged hydrochloric acid was effected in earthenware pipes, whilst the residual 5 per cent to 10 per cent of chlorine gas was dried in sulphuric acid prior to absorption in slaked lime.

Several technical difficulties were inherent in the earlier plants, notably the loss of most of the " pan acid " and all the " roaster acid " from the Leblanc process, the impossibility of obtaining a continuous supply of gas, the rapid poisoning of the catalyst, and the very indifferent yields obtained.

Hasenclever, in 1883, introduced the method of purifying the hydrochloric acid by absorption in water and blowing the purified gas out again by air in the presence of sulphuric acid. A sulphuric acid drier for the gases prior to passage through the superheater was simultaneously introduced. By this method a continuous supply of pure gases free from poisons such as sulphuric acid, $FeCl_2$,SO_2,As_2O_3, and carbon dioxide was thus obtained. The life of the catalyst was extended to from ten to twelve weeks, and more than 12 tons of bleaching powder could be prepared with the loss of only 1 ton of impregnated clay. Subsequent improvements in the yield were made as a result of the investigations of J. H. Harker,[1] Lunge and Marmier,[2] G. N. Lewis,[3] and Vogel v. Falckenstein.[4]

It was evident that the process involved the partition of hydrogen between oxygen and chlorine, the reaction

$$4HCl + O_2 \rightleftarrows 2Cl_2 + 2H_2O$$

being strictly reversible. Also the function of the cuprous chloride was shown to be purely catalytic in establishing the equilibrium at the temperature of operation.

The values of the equilibrium constant $K = \frac{C^2_{H_2O} \cdot C_{Cl_2}{}^2}{C^4_{HCl} \cdot C_{O_2}}$ at different temperatures were investigated, using the dynamic method by von Falckenstein, who passed different gas mixtures of the four constituents over cupric chloride and platinic chloride catalysts, maintained at suitable temperatures in an electric furnace. G. N. Lewis utilised the static method, obtaining equilibrium when commencing with mixtures of hydrochloric acid and oxygen.

The following results were obtained :

Temperature.	log K.
352°	2·43
356	1·90
419	1·52
450	1·40
600	0
650	−0·4

[1] *Zeitsch. physikal. Chem.*, 1892, **9**, 673.
[2] *Zeitsch. angew. Chem.*, 1897, 108.
[3] *J. Amer. Chem. Soc.*, 1906, **28**, 1380.
[4] *Zeitsch. physikal. Chem.*, 1909, **65**, 371.

If the heat of reaction Q (13,800 cals.) be assumed to be independent of the temperature, Lewis showed that the values of K at various temperatures could be calculated from the following equation :

$$\log_{10} K = \frac{6036}{T} - 7{\cdot}244.$$

The reaction may of course be considered as the combination of two simpler reactions :

$$2H_2O \rightleftarrows 2H_2 + O_2,$$
$$2HCl \rightleftarrows H_2 + Cl_2;$$

if $$K_1 = \frac{p^2_{H_2} \cdot p_{O_2}}{p^2_{H_2O}} \text{ and } K_2 = \frac{p_{H_2} \cdot p_{Cl_2}}{p^2_{HCl}},$$

then $$\log_{10} K = 2 \log_{10} K_2 - \log_{10} K_1.$$

Adopting Nernst and Wartenberg's figures for the dissociation of water vapour at high temperatures :

$$\log_{10} K_1 = \frac{25050}{T} + 1{\cdot}75 \log_{10} T + 0{\cdot}00028\ T - 0{\cdot}2,$$

and employing for K_2 the value from the corresponding investigations of Dolezalek and Löwenstein on the dissociation of hydrochloric acid :

$$\log_{10} K_2 = -\frac{9626}{T} - 0{\cdot}8,$$

it follows that

$$\log_{10} K = \frac{5790}{T} - 1{\cdot}75 \log T - 0{\cdot}00028\ T - 1{\cdot}4.$$

Either of the above equations gives values of K which approximate very closely to the observed values. Nernst [1] gives the following calculated values, in close agreement with the determinations of v. Falckenstein :

Temperature.	$\log T$.
450°	1·50
600	− 0·009
650	− 0·430

The fractional conversion of hydrochloric acid in dry air into chlorine can be calculated in a similar manner to that detailed in the oxidation of sulphur dioxide by the contact process. If x be the percentage of the hydrochloric acid, it is easily seen that

$$\sqrt[4]{K} = \frac{C^{\frac{1}{2}}_{H_2O} \cdot C^{\frac{1}{2}}_{Cl_2}}{C_{HCl} \cdot C^{\frac{1}{2}}_{O_2}} = \frac{x}{2(1-x)C^{\frac{1}{2}}_{O_2}}.$$

Excess of oxygen is thus beneficial to the yield of chlorine, but the conversion is not appreciably affected by slight alterations in the air

[1] *Application of Thermodynamics to Chemistry*, 89.

upply owing to the dependence of the equilibrium on the fourth root f the oxygen pressure only.

The increase in the values of K with decrease in temperature pointed o the necessity of finding suitable catalytic material for increasing the eaction velocity at low temperatures. No catalyst has as yet been ound superior or even equal to Hurter and Deacon's cuprous chloride. Vith pumice impregnated with cuprous chloride Lunge and Marmier ound that catalysis was already commencing at 310°, but the reaction elocity was still very slow below 400°. At 450°-460° the reaction elocity is sufficiently rapid to give a satisfactory yield under technical orking conditions.

Hurter suggested the use of cuprous chloride from a survey of the eats of formation of the chlorides and oxides of the various elements, nowing that no other element except copper formed oxides and hlorides in which the combination was of so loose a character.[1] The echanism of the reaction according to Deacon is based on the following ycle :

$$2CuCl_2 = Cu_2Cl_2 + Cl_2,$$
$$Cu_2Cl_2 + O = CuO \,.\, CuCl_2,$$
$$Cu_2Cl_2O + 2HCl = 2CuCl_2 + H_2O.$$

evi and Bettoni, as the result of a series of experiments with various atalysts,[2] such as $CuCl_2$, $CuSO_4$, $MnCl_2$, $MgCl_2$, and hot pumice, rrived at the conclusion that the extraction of water was the chief nction of the catalyst, and that temporary hydrate formation played an nportant rôle in the process :

$$CuSO_4 + 2HCl + O_2 = CuSO_4,H_2O + Cl_2,$$
$$CuSO_4,H_2O = CuSO_4 + H_2O.$$

ubsequently the oxychloride, $CuO \,.\, CuCl_2$, was isolated and the original ews of Deacon and Hurter received further support in the discovery at most substances capable of forming oxychlorides were catalytically tive. There is some evidence, however, that the whole of the talyst is not converted to the oxychloride at any stage in the ocess, suggesting that the oxide ion enters here and there into e lattice of the cuprous chloride, and is then again replaced.

V. Falckenstein drew attention to the necessity of carefully drying e gases before catalysis, and he showed that if the effluent gases ere dried by sulphuric acid and again passed through the catalyst the nversion would rise from 82·5 to 85 per cent, and on a further passage 88 per cent, owing to the shifting of the equilibrium ratio, $\frac{HCl}{Cl_2}$, by e abstraction of the water formed during the reaction.

[1] *J. Soc. Chem. Ind.*, 1883, 2, 106.

[2] *Gazzetta*, 1905, **351**; 320.

The two technical difficulties associated with the use of cuprou chloride as a catalyst are its sensitiveness to poisons and its volatilit at the lowest working temperature, 450°.

Hasenclever's method of purification of the hydrochloric acid effec a very considerable improvement in the purity of the gas, but sulphu dioxide, as well as sulphuric acid spray, are not entirely eliminate Kolb, in 1891, suggested the further purification by passage over hc salt maintained at 450°, whereby sodium sulphate was formed, and small additional quantity of hydrochloric acid would pass on with th main gas stream.

Less volatile but more inefficient catalysts than cuprous chlorid have been proposed from time to time, but owing to the bad yield resulting from the higher temperatures employed they have not foun technical application.

Amongst the more important may be mentioned ferric chloride suggested by Thibierge in 1855, and platinised asbestos, by Weldor 1871. Hargreaves and Robinson (1872) suggested chromic oxide De Wilde and Reychler mixtures of manganese and magnesiur chlorides, in which a complex oxide was assumed to be an intermediar in the cycle of reactions :

$$3MgCl_2 + 3MnCl_2 + 4O_2 = Mn_3Mg_3O_8 + 6Cl_2,$$
$$Mn_3Mg_3O_8 + 16HCl = 3MgCl_2 + 3MnCl_2 + 8H_2O + 2Cl_2.$$

Ditz and Margosches, in 1904, employed the chlorides of the rare earths whilst Dieffenbach, in 1908, suggested the double chlorides of coppe and other elements.

Mond [1] put forward a somewhat ingenious scheme to obtain mor concentrated chlorine gas than that obtained in the usual Deacon process. If air and hydrochloric acid be passed alternately over heate nickel oxide deposited on pumice, the oxidation of the hydrochlori acid can be made a two-stage process through the intermediary forma tion of nickel chloride, which is reconverted into the oxide by the air The idea does not seem to have been developed.

The Weldon process.—In 1869 W. Weldon [2] introduced, at St. Helens a process for the oxidation of hydrochloric acid in solution. At one tim the process had a very considerable industrial importance, but i now being supplanted by modifications of the Deacon process alread described.

Weldon's process suffers from the disadvantage that nearly 60 pe cent of the original hydrochloric acid is lost in the form of calciun chloride, in addition to 3 per cent by weight, on the chlorine obtained of the catalyst, manganese dioxide (pyrolusite); but its developmen was doubtless due to the great advantage it possessed over the Deacon process, in that the chlorine gas evolved was very concentrated. Th

[1] B.P. 17272/1889. [2] B.P. 8308/1886.

method of technical operation is as follows: hydrochloric acid, approximately 30 per cent strength, is first oxidised by means of manganese dioxide:

$$MnO_2 + 4HCl = MnCl_2 + Cl_2 + 2H_2O.$$

The spent manganese chloride solution is then carefully neutralised with limestone, and after removal of any ferric hydroxide by precipitation, is made alkaline by the addition of milk of lime, 30 per cent in excess of that required to precipitate all the manganous hydroxide being added:

$$MnCl_2 + Ca(OH)_2 = Mn(OH)_2 + CaCl_2.$$

The Weldon "mud" is now aerated at 50°-60° for several hours, calcium manganate being finally precipitated:

$$2Mn(OH)_2 + O_2 + Ca(OH)_2 = CaO \,.\, 2MnO_2 + 3H_2O.$$

On the addition of more manganous chloride and lime during the process of aeration, a further oxidation ensues:

$$2CaO \,.\, MnO_2 + 2Ca(OH)_2 + 2MnCl_2 + O_2 = 2(CaO \,.\, 2MnO_2) + 2CaCl_2 + 2H_2O.$$

It will be noted that when the regenerated manganese dioxide is used for the oxidation of a fresh quantity of hydrochloric acid a very considerable quantity of free base has first to be neutralised, thus again lowering the conversion efficiency of the process.

The mechanism of the process depends essentially on the use of the manganese salt as an oxygen carrier. Although we can show from the previous considerations in the Deacon process that atmospheric oxygen should be able to displace the chlorine from even weak solutions of hydrochloric acid, no active catalyst for this reaction has yet been found. If we extrapolate from v. Falckenstein's figures, the probable value of $K = \frac{[H_2O][Cl_2]}{[HCl]^2[O_2]^{1/2}}$ at 0°, we obtain a value of $K = 10^7$. The solubility of chlorine gas under 1 atmosphere is about 1 grm. per litre, and of oxygen under two-fifths of an atmosphere 0·007 grm. per litre, or $\frac{[Cl_2]}{[O_2]^{1/2}}$ in a liquid saturated with both gases at the respective pressures $= \frac{1}{0{\cdot}085}$ approximately. Hence $\frac{[H_2O]}{[HCl]^2} = 10^7 \times 0{\cdot}085 = Ca10^6$. That is to say, the dilution below which atmospheric oxygen would be inoperative in displacing chlorine from hydrochloric acid is remarkably small.

Weldon relied upon the preparation of a more active oxidising agent than atmospheric oxygen, so that the oxidation of the acid might proceed at reasonable velocities. The method by which the oxidising power or oxidising potential of atmospheric oxygen is raised above its

normal value at the expense of the energy lost in the combination of the acid with the free alkali, is an interesting one.

We may write the oxidation reaction as follows :

$$MnO_2 + 2H_2O \rightleftarrows Mn(OH)_2 + 2(OH)' + 2\oplus \rightleftarrows Mn^{\cdot\cdot} + 2(OH)' + 2(OH)' + 2\oplus.$$

The potential difference between an (MnO_2) electrode immersed in the Weldon mud and the solution itself is given by the equation

$$E = E_0 + \frac{RT}{2\epsilon} \log \frac{[MnO_2][H_2O]^2}{[Mn^{\cdot\cdot}][OH']^4} = E'_0 + \frac{RT}{2\epsilon} \log K \frac{H^{\cdot 4}}{Mn^{\cdot\cdot}},$$

since $[MnO_2]$ and $[H_2O]$ can be assumed to be constant.

If this electrode be coupled up with an auxiliary oxygen electrode in a neutral solution, neglecting the P.D. at the boundary of the Weldon mud and the electrolyte surrounding the oxygen electrode, the E.M.F. of the cell thus set up is obtainable from the following relationship :

$$\begin{array}{ccccc} PtO_2 & | & Mn(OH)_2 & | & MnO_2Pt \\ & \overset{\vee}{E_1} & & \overset{\vee}{E_2} & \end{array}$$

$$V = E_1 - E_2 = E_0 + \frac{RT}{2\epsilon} \log \frac{C_{O''}}{\sqrt{p_{O_2}}} - E'_0 - \frac{RT}{2\epsilon} \log \frac{H^{\cdot 4}}{Mn^{\cdot\cdot}}.$$

The value of E_0 is approximately 1·22 volts, taking p as 1 atmosphere and a neutral electrolyte.

The value for E'_0 can be obtained from the investigations of Tower,[1] Inglis,[2] and Haehnel,[3] and may be taken as equal to the value $E'_0 = 1{\cdot}35$ volts.

Hence :

$$E_1 - E_2 = 1{\cdot}22 - 1{\cdot}35 + \frac{RT}{2\epsilon}\left(\log H^{\cdot 2} - \log \frac{H^{\cdot 4}}{Mn^{\cdot\cdot}}\right)$$

$$= -0{\cdot}13 + \frac{RT}{2\epsilon} \log \frac{Mn^{\cdot\cdot}}{H^{\cdot 2}} = -0{\cdot}13 + \frac{RT}{2\epsilon} \log Mn^{\cdot\cdot}(OH')^2 \cdot \frac{1}{c^2},$$

where c is the value of the product $C_{H^\cdot} \cdot C_{OH'} = C_{H^\cdot}{}^2$ in pure water.

In a neutral solution the solubility coefficient $Mn^{\cdot\cdot}(OH')^2 = 4 \times 10^{-14}$ approximately.

Hence :

$$E_1 - E_2 = -0{\cdot}13 + 0{\cdot}029 \log \frac{4 \times 10^{-14}}{(0{\cdot}5 \times 10^{-14})^2} = -0{\cdot}13 + 0{\cdot}45 = 0{\cdot}32 \text{ volt.}$$

In a similar manner we can calculate the P.D. of the cell in normal hydrion concentration and with a normal $Mn^{\cdot\cdot}$ concentration :

$$V = -0{\cdot}13 + \frac{RT}{2\epsilon} \log Mn^{\cdot\cdot} - \frac{RT}{2\epsilon} \times 2 \log H^{\cdot} = -0{\cdot}13.$$

[1] *Zeitsch. physikal. Chem.*, 1895, **18**, 17, 18. [2] *Zeitsch. Elektrochem.*, 1903, **99**, 226.
[3] *Ibid.*, 1909, **15**, 834.

For a normal $Mn^{\cdots\cdot}$ concentration the P.D. would obviously be much greater.

Thus in acid solutions the oxidising potential of the MnO_2 electrode exceeds that of atmospheric oxygen and necessarily that of chlorine, since in n-hydrion concentration the cell, $PtO_2 \mid Cl_2 \mid Pt$, has an E.M.F.

$$V_1 = V_0 + \frac{RT}{2\epsilon} \log \frac{p_{O}'' p_{Cl_2}}{\sqrt{p_{O_2}(p_{Cl'})^2}} = 1{\cdot}493 - 1{\cdot}35 = 0{\cdot}14 \text{ volt},$$

indicating that the manganese " mud " has an oxidising potential at least 0·27 volt higher than the liberated chlorine, thus giving a measure of the energy available for oxidation of the hydrochloric acid. In neutral solutions the manganese " mud " possesses an oxidising potential inferior to that of oxygen or of chlorine.

In actual practice more alkali has to be added than is necessary to ensure the oxidation of the manganous salt. In the early experiments of Weldon, red solutions were occasionally obtained during the process of oxidation, and it was found that the quantity of manganese dioxide formed during aeration was very small. It was finally shown that the red colour was due to the formation of manganous manganic oxide, owing to a deficiency of base, according to the interaction

$$MnO_2 + \tfrac{1}{2}H_2O \rightleftarrows \tfrac{1}{2}Mn_2O_3 + OH' + \oplus,$$

where

$$E = E_0 + \frac{RT}{\epsilon} \log \frac{(MnO_2)(H_2O)^{\frac{1}{2}}}{(Mn_2O_3)^{\frac{1}{2}}(OH')}$$

or

$$E = E_0 + \frac{RT}{\epsilon} \log C\frac{H^{\cdot}}{Mn^{\cdots}}.$$

Other processes for the oxidation of hydrochloric acid.—Owing to the inefficiency of the Weldon process from the yield point of view, the inventor and Péchiney experimented for many years on the production of chlorine by the aid of the following cyclic process :

$$4MgCl_2 + 2H_2O + O_2 = 4MgO + 4HCl + 2Cl_2,$$
$$MgO + 2HCl = MgCl_2 + H_2O.$$

A pure magnesium chloride was not utilised, but the crude liquor after evaporation was mixed with the required amount of powdered magnesia to form the oxychloride, $MgO \,.\, MgCl_2$, prior to drying at 300°. The chlorine and hydrochloric acid together with some steam were removed by an air blast at 1000°.

Another ingenious process which has been the subject-matter of various patents involves the following cyclic process, in which oxides of nitrogen play the part of catalysts, as in the sulphuric-acid lead-chamber process :

$$3HCl + HNO_3 = Cl_2 + NOCl + 2H_2O,$$
$$HNO_3 + NOCl = N_2O_4 + HCl,$$
$$N_2O_4 + 2HCl = N_2O_3 + H_2O + Cl_2,$$
$$N_2O_3 + O_2 + H_2O = 2HNO_3.$$

This idea, developed by Dunlop in 1849, together with the Weldon-Péchiney process outlined above, does not appear to have received any considerable technical development.

The Fractional Combustion of Hydrogen Sulphide

We have already indicated the technical significance of the catalytic processes employed for the oxidation of sulphur dioxide to sulphuric anhydride. A great part of the dioxide utilised for this purpose is derived from the combustion of natural sulphides, especially pyrites and blende, or from artificial sulphides such as gas-works spent oxide, yet a certain quantity is always obtained from the combustion of elementary sulphur. In 1882 Claus introduced a method for the fractional combustion of hydrogen sulphide into sulphur and water, thus preparing sulphuric acid by a three-stage process:

$$(1) \quad 2H_2S + O_2 = 2H_2O + 2S,$$
$$(2) \quad 2S + 2O_2 = 2SO_2,$$
$$(3) \quad 2SO_2 + O_2 + H_2O = H_2SO_4.$$

It has been suggested that the combustion of hydrogen sulphide to sulphur dioxide could be accomplished in one stage, which, in the presence of excess of air, could be used directly for the preparation of sulphuric acid. This idea does not seem to have received any technical development, chiefly on account of the very large quantities of diluent nitrogen present in the resulting sulphur-dioxide gas mixture.

The Claus process, however, in the hands of A. M. Chance, has been developed, and at the present time is the most satisfactory method of dealing with the alkali waste of the Leblanc soda process.

Alkali waste contains some 40 per cent of calcium sulphide, 20 per cent of calcium carbonate, and 10 per cent of lime, the residue consisting chiefly of silicates with small quantities of sodium carbonate and iron sulphate. Chance modified Gossage's (1838) process for the production of a gas rich in sulphuretted hydrogen by decomposition with carbon dioxide. Carbon dioxide from lime-kilns is passed through a set of carbonating towers through which a suspension of alkali waste flows in the counter-current direction. In the first tower sulphuretted hydrogen is evolved according to the equation

$$CaS + H_2O + CO_2 = CaCO_3 + H_2S.$$

The hydrogen sulphide diluted with the nitrogen in the original kiln gas passes to the second tower, in which the hydrogen sulphide is absorbed, with the formation of calcium hydrosulphide:

$$CaS + H_2S = H_2CaS_2.$$

On carbonating this solution a gas containing twice as much hydrogen sulphide as was obtained from the first tower is evolved and collected in gas-holders over water covered with a layer of oil.

The sulphuretted hydrogen thus obtained, of about 38 per cent purity, is mixed with air in the proportion of 5 volumes of gas to 4 volumes of air and passed into the Claus kiln for fractional combustion into sulphur and water vapour.

The Claus kiln consists essentially of a fire-brick cylinder containing a grating on which the catalytic material, usually bog iron ore (hydrated ferric oxide ignited at a low temperature), is deposited. The combustion is started by throwing a little red-hot coal into the furnace and is maintained by the heat of the reaction itself. The temperature of the eflowing gases, one foot from the kiln, should not exceed 300°, otherwise a loss of sulphur occurs. The hot gases are subsequently passed into a series of condensing chambers, where part of the sulphur condenses to the liquid state, and the rest is recovered as flowers of sulphur in the condensed steam.

In order to minimise the loss of sulphur compounds (H_2S or SO_2) in the effluent gases, the exact theoretical ratio, $H_2S : O_2$, required for combustion in the entering gases must be maintained. The temperature of the catalyst is mainly determined by the speed of passage of the gas.[1]

Various other catalytic materials for this combustion process have been utilised, such as broken fire-brick, bauxite, and dried Weldon mud. There are, however, two distinct advantages in making use of an active catalyst which will operate at low temperatures. First, the life of the kiln and the condensing chambers is considerably shortened by high temperature operation, and, secondly, above 200° an interesting reverse reaction between the sulphur and the steam formed begins to take place with appreciable velocity :

$$2H_2O + 3S \rightleftarrows 2H_2S + SO_2.$$

It is extremely probable that the flowers of sulphur recovered in the condensed water do not originate in the original condensate of sulphur vapour from the combustion process, but result from the interaction in solution of the sulphur dioxide and hydrogen sulphide formed in the lower parts of the kiln and in those condensers which are above 100° to 200°.

The catalytic activity of oxides of iron and manganese in the Claus process is usually attributed to the property these elements have of forming more than one oxide, thus permitting the assumption of an oscillating oxide acting as oxygen carrier :

$$\begin{array}{ccccc} Fe_2O_3 & \longleftarrow & O_2 & \longrightarrow & O_3Fe_2 \\ \downarrow & & \uparrow & & \downarrow \\ H_2S & \longrightarrow & Fe_2O_2 & \longleftarrow & H_2S. \end{array}$$

Some experiments by the writers, however, indicate that iron sulphide is an intermediary compound in the process of oxidation, and that the

[1] See, however, Carpenter and Linder, *J. Soc. Chem. Ind.*, 1903, 22, 457 ; 1904, 23, 557.

mechanism of oxidation can be more truly represented on the following lines, making the Claus process simply an extension of the ordinary gas-works process of spent oxide revivification:

$$Fe_2O_3 + 3H_2S \rightleftarrows 2FeS + 3H_2O + S,$$
$$4FeS + 3O_2 \rightleftarrows 2Fe_2O_3 + 4S.$$

Catalysis in the Purification of Illuminating Gas and Gaseous Fuels

As is well known, illuminating gas after leaving the scrubbers contains various quantities of substances which are deleterious in the uses to which the gas is subsequently put: Thus, in addition to substances like carbon dioxide, which lower the illuminating power and calorific value of the product, the scrubbed gas may contain anything from 0·5 to 2·0 per cent of sulphuretted hydrogen as well as organically combined sulphur compounds, such as carbon disulphide, thiophene, and mercaptans, to the extent of 10 to 80 grains of sulphur per 100 cubic feet of gas. Such sulphur compounds, since, on combustion, they yield sulphur dioxide, are disagreeable constituents of the final product. Their removal is consequently desirable. Indeed, the removal of free sulphuretted hydrogen is required by statutory regulation. Formerly, also, the removal of the combined sulphur to a certain degree was also required by statute, but this is no longer required.

In practice it is the custom to free illuminating and other gases from sulphuretted hydrogen by passing them through various suitably moistened absorbent materials, among which the more commonly employed are lime, oxide of iron, and manganese dioxide in the form of Weldon mud. The former removes both carbon dioxide and the sulphuretted hydrogen, together with a fraction of the carbon disulphide present. Its use, however, is becoming more and more restricted, especially to small undertakings having a local market for the product, since the disposal of the spent lime, containing both carbonate and a sludge of calcium sulphide, is both difficult and disagreeable, owing to the obnoxious odour which the material possesses. The oxides of iron and manganese are increasingly used, and in a manner which involves their functioning as catalysts.

The elimination of sulphuretted hydrogen by means of oxide of iron is carried out in huge boxes carrying the absorbent material. This is generally employed in the form of bog iron ore, which, from its content of organic matter, is porous and thus favours ready transformation to sulphide. If the precipitated hydroxide be employed, the material is generally lightened by admixture with organic matter in the form of sawdust. The material is at all times kept suitably moist. Absorption of the sulphuretted hydrogen involves a change of the absorbent from the brownish hydrated oxide to the blackish-green

sulphide. Ferric sulphide and ferrous sulphide and sulphur are the products of the transformation, which may be symbolised by the equations

$$Fe_2O_3 + H_2O + 3H_2S = Fe_2S_3 + 4H_2O,$$
$$Fe_2O_3 + H_2O + 3H_2S = 2FeS + 4H_2O.$$

After absorption ceases, the sulphides, by exposure to air, may be transformed into the original material with the simultaneous production of sulphur, which change may be represented by the equations

$$2Fe_2S_3 + 3O_2 = 2Fe_2O_3 + 6S,$$
$$4FeS + 3O_2 = 2Fe_2O_3 + 4S.$$

Thus, by alternation of the process of absorption and of exposure to air, or revivification, the original oxide of iron may effect the catalytic conversion of the sulphuretted hydrogen to sulphur and thereby the removal of the sulphur from the gas. As much as 50 per cent of sulphur may thus be accumulated in the oxide by alternation of the two stages, and the resultant material is then a convenient source of sulphur for sulphuric acid manufacture.

In actual operation under working conditions, illuminating gas generally contains small amounts of oxygen entering the gas through leakages in the system. This oxygen effects, to a certain degree, in the boxes, the process of revivification attained otherwise by exposure to air. The observation of this action of oxygen has led to a development of modern gas purification in which the oxygen content of the gas at the entrance to the oxide purification system is controlled, and, if necessary, air is added to the gas to be purified to facilitate the process of revivification *in situ*. Thus, the process of purification becomes in essence the catalytic conversion, by means of oxide of iron acting as catalyst, of sulphuretted hydrogen and oxygen to sulphur and water, according to the equation

$$2H_2S + O_2 = 2H_2O + 2S + 110{,}000 \text{ cals.}$$

The advantage to be obtained from the admission of air to the purification system is that the purifiers can be worked for much longer periods without recharging. In modern gas-works practice this period may amount to as much as six months per box with a system of purification employing four boxes in series. The amount of oxygen added is restricted by two factors, the diluent effect on the gas of the nitrogen simultaneously added and the fact that the heat effect of the reaction may be so great locally as to cause combustion of the material in the purifiers, with consequent introduction of sulphur dioxide into the gas and disorganisation of the purification system. The care requisite in this regard will readily be appreciated by the gas engineer who has knowledge of the strongly exothermic nature of the reaction, which, as given in the equation above, amounts to 110,000 cals.

Precipitated oxide of iron, an artificially prepared material, has

come into considerable use as the catalytic material, since its action is found to be more vigorous than the natural bog iron ore. For similar reasons, the manganese dioxide of Weldon mud is also employed, its reactivity with sulphuretted hydrogen being computed to be five times that of the bog ore. All the materials are employed until so far loaded with sulphur that they are available as an economical source of sulphur.

It is to be pointed out that all the fuel gases of industry contain greater or less amounts of sulphuretted hydrogen, and are therefore potential sources of sulphur supply for the sulphuric acid industry. The gases from by-product coking ovens are also a further such source. Since, however, the capital outlay in plant and space for oxide box purification is considerable, the economy of the purification process is small, and these sources of sulphur have to a marked degree been neglected, the sulphur being left in the gas with consequent vitiation of the atmosphere in the neighbourhood of their combustion. It is to be hoped that further improvement may be effected in the recovery of sulphuretted hydrogen from all fuel gases, so as to render its removal a sound economic proposition and thereby minimise the dependence of the community for sulphur upon foreign sources of supply.

The elimination of sulphuretted hydrogen from coal gas by the methods just outlined is remarkably complete, and with skilled supervision the quantities of such gas in modern illuminating gas are negligible. The process, however, except when lime is employed, fails to bring about the removal of the organically combined sulphur compounds, and, in the case of lime, only partial removal of carbon disulphide is effected. Attempts to eliminate organically combined sulphur are almost as old as the illuminating gas industry itself, and as many of the suggested processes are catalytic in nature their record is essential here.[1] So far back as 1806 Edward Heard suggested passing the crude gas over alkaline earth or certain metals or their oxides placed in iron tubes or other vessels and exposed to a furnace. In 1818 Palmer took out patents upon a process of removal by passage of the crude coal gas through heated tubes containing iron, oxide of iron, or iron stone, so disposed as to present as large a surface as possible. In the 'fifties Thompson suggested a process to operate upon a technical scale, of which the principle is merely to pass the gas over lime heated to a dull red or much lower, or small pieces of brick or pumice-stone previously steeped in a solution of the chloride of platinum. Bowditch, in 1860, patented a process for removal of combined sulphur by passing the gas first freed from sulphuretted hydrogen in the ordinary manner through heated clay, oxide of iron, or lime, the temperature found most efficient being between 140° and 215°. In 1870 Vernon Harcourt proposed to decompose organic sulphur compounds by placing a mass of iron turnings or wire into the mouthpiece of each retort or by conducting the gas through heated tubes partially

[1] Carpenter, *Purification of Gas by Heat.*

filled with suitable surface-presenting material, and a trial was made in 1874 of the process suitably modified for technical operation. I. von Quaglio, in 1878, proposed the use of heated clay balls impregnated with the chloride of a metallic catalyst, or such metals themselves in powdered form.

All these processes are in reality suggestions for conducting readily by means of catalytic agents a reaction which may be illustrated best with reference to carbon disulphide by means of the equation

$$CS_2 + 2H_2 = 2H_2S + C.$$

Upon the laboratory scale this is readily effected and forms the basis of the Harcourt test for such sulphur compounds. As actually operated in the test, the gas is passed through a heated flask containing platinised pumice. The disulphide is decomposed quantitatively, and the formation of sulphuretted hydrogen determined by means of a colour test.

The installation of such a process of purification upon a large technical scale for the purification of illuminating gas is due to Hall and Papst, of the Portland Gas and Coke Co., Oregon, U.S.A. The device patented by Hall for the purpose is composed of two heaters filled with chequer-work as in a water-gas plant, and a generator from which they are heated internally and alternately by producer gas. Whilst the coal gas is being treated for sulphur compounds in the one heater, the other is being heated up by the gas from the generator, and so continuity of purification is ensured. During 1909 as many as 817 million cubic feet of gas were heated in this way at an average cost stated to be ½d. per 1000 cubic feet. The percentage reduction of combined sulphur in the gas throughout the year averaged 70 per cent, reducing the content from an average of 59 grains to 17 grains per 100 cubic feet. The temperatures employed were high (up to 900° is suggested), so that doubtless there would be an accompanying loss in illuminating power. The percentage reduction increased with increasing temperature, varying from 20 per cent at 427° to 76 per cent at 704°.

The work of Carpenter and Evans[1] in England upon similar lines may now be detailed. A variety of catalytic materials for the decomposition of the organic sulphur by means of hydrogen were studied with a view to their application upon a practicable scale. Among such materials may be mentioned fire-brick, pumice, iron oxide, platinum, and nickel. Of the contact materials studied, pumice or fire-clay impregnated with finely divided nickel was chosen as the most suitable, being the most active and not prohibitive in cost. After smaller scale experiments, a large-scale plant with a capacity of 1¾ million cubic feet per day was erected. This was later supplemented by a plant

[1] Carpenter, *J. Gas Lighting*, 1914, **126**, 928; Evans, *J. Soc. Chem. Ind.*, 1915, **34**, 9.

dealing with 10 million cubic feet per day in London and one at East Greenwich in five units, each unit capable of dealing with 3 million cubic feet of gas per day. The gas to be heated is previously freed from sulphuretted hydrogen in the usual way and passes through a system of preheaters and heat interchangers to the reaction chamber, maintained at 450°, at which temperature approximately 80 per cent conversion of the sulphur compounds may be obtained. The heated gas leaving the reaction chamber flows through the heat exchangers in the contrary direction, and permits therefore of economy in the heat required to be added to the system. In the East Greenwich plant the weight of metallic nickel employed is 1321 lbs., equivalent approximately to 1 lb. of metallic nickel per 10,000 cubic feet of gas per day. The daily consumption of coke for the same plant amounts to $5\frac{1}{2}$ tons per day. Provision is made for regeneration of the catalytic material after a period of use. This is necessary owing to the deposition of carbon resulting from the reaction in the catalytic material employed. Regeneration is effected by blowing hot air through the system, which burns off the carbon deposit from the fire-clay ball impregnated with nickel. The average reduction of sulphur content in the 10 million cubic feet per day plant over a period of sixteen months was from 40 to 8 grains per 100 cubic feet, or a percentage reduction amounting to 80 per cent. The effective reduction is to a certain degree governed by the sulphur content of the gas, a maximum reduction, equivalent to 84 per cent, being observed on a gas of 64 grains of sulphur per 100 cubic feet, the minimum being 72 per cent on a gas of 19 grains sulphur content. The effect of the process on the illuminating power of a rich 20-candle-power gas was specially studied. It was found that the illuminating power was unimpaired, the average quality before and after treatment for sulphur being 20·54 and 20·46 candles respectively. The cost of working the sulphur extraction process is given as 0·3d. per 1000 cubic feet, including fuel, maintenance charges, depreciation, and interest. The capital cost works out at £1500 per million cubic feet of gas per day.

It is possible that yet another catalytic reaction may be employed technically, in the future, for removal of the combined sulphur from fuel and illuminating gases. It is well known that carbon disulphide reacts at suitable temperatures with water to form carbon dioxide and hydrogen sulphide, according to the equation

$$CS_2 + 2H_2O = CO_2 + 2H_2S.$$

In a French process patented by Guillet[1] this reaction is accelerated catalytically by means of oxide of iron maintained at temperatures between 80° and 300°. Reduction on a laboratory scale from 16 to 4·3 grains per 100 cubic feet was claimed at 130°.

The sulphuretted hydrogen formed is fixed, however, by the iron

[1] *Soc. Tech. de l'Ind. du Gaz en France*, 1912, p. 245.

oxide, and hence the process, conducted in the above manner, must necessarily be discontinuous. On the other hand, it is known, for example, that in the catalytic hydrogen process employing water gas and steam at 500° with iron oxide as basic catalytic material, all sulphur compounds are converted to hydrogen sulphide in the course of the reaction and pass on as such with the other products. It does not seem unlikely, therefore, that such a catalytic process for sulphide removal could be operated continuously if the right conditions were obtained. The reaction would possess a point of advantage over the processes previously considered, since carbon dioxide, and not carbon, is the product of conversion. The catalytic mass, therefore, would remain unaltered and the process of aeration requisite in the Hall and Papst and in the Evans-Carpenter processes would be unnecessary. Interesting technical developments of the process of M. Guillet may therefore be expected.

The Influence of Catalysts in Surface Combustion

During recent years a considerable advance has been made in the technical application of the catalytic process of surface combustion by Schnabel in Germany, but more especially by Bone and his co-workers in England.[1]

In the preceding pages we have already discussed the catalytic activity of certain substances, notably platinum, in promoting the combination of oxygen and hydrogen as well as other combustible gaseous mixtures, and have noted that under suitable conditions the catalytic material can attain quite high temperatures. Thus Fletcher[2] appears to have been the first to study the conditions necessary to maintain the catalyst at a high temperature by the process of surface combustion. This investigator showed that it was possible by suitable regulation of the composition of a mixture of coal gas and air to keep a ball of iron wire continuously at a high temperature without any combustion taking place in the form of flame, provided that the gaseous mixture came in direct contact with the hot material.

Bone, in 1902, commenced a systematic investigation on the influence of various catalytic materials such as platinum, gold, silver, copper, and nickel oxides, and magnesia at fairly elevated temperatures, *circa* 500°.

He noted that there was a steady increase in catalytic activity with elevation of the temperature and that the disparity between different catalytic materials diminished with ascending temperatures.

As a logical sequence to these earlier experiments, the conditions necessary for maintaining a catalytic material continuously and

[1] *Phil. Trans.*, 1906 (*A*), 206; *Ber.*, 1913, **46**, 5; *Proc. Amer. Gas Inst.*, 1912, **6**, 564; R.I. Lecture, Feb. 1914.

[2] *J. Gas Lighting*, 1887, **1**, 168; see Bone, *loc. cit.*

uniformly at a high temperature by surface combustion were developed.

Bone and M'Court's earliest types of apparatus consisted essentially of a porous fire-brick diaphragm through which a gas and air mixture in the correct ratio for complete combustion was forced by a suitable injector or blower. The fire-brick diaphragm rapidly attains a bright-red heat and complete combustion is effected in a very thin layer of the diaphragm ($\frac{1}{8}$ to $\frac{1}{4}$ inch). The advantages of such a heater, viz. the high efficiency in the production of effective radiant energy and the possibility of fixing the diaphragm in any position, are partly gainsaid by the necessity of using either air or gas under pressure, and by the fact that the diaphragms are slowly but continuously blocked up by dust and tar fog in the air or gas.

As a consequence the surface combustion heater was modified by substituting a bed of refractory granular material for a diaphragm and forcing through it a suitable mixture of air and gas or vaporised fuel. Many applications of this method have given extremely successful results in practice. Thus the granular material may be packed round muffles, crucibles, or retorts or the flue tubes of steam boilers.

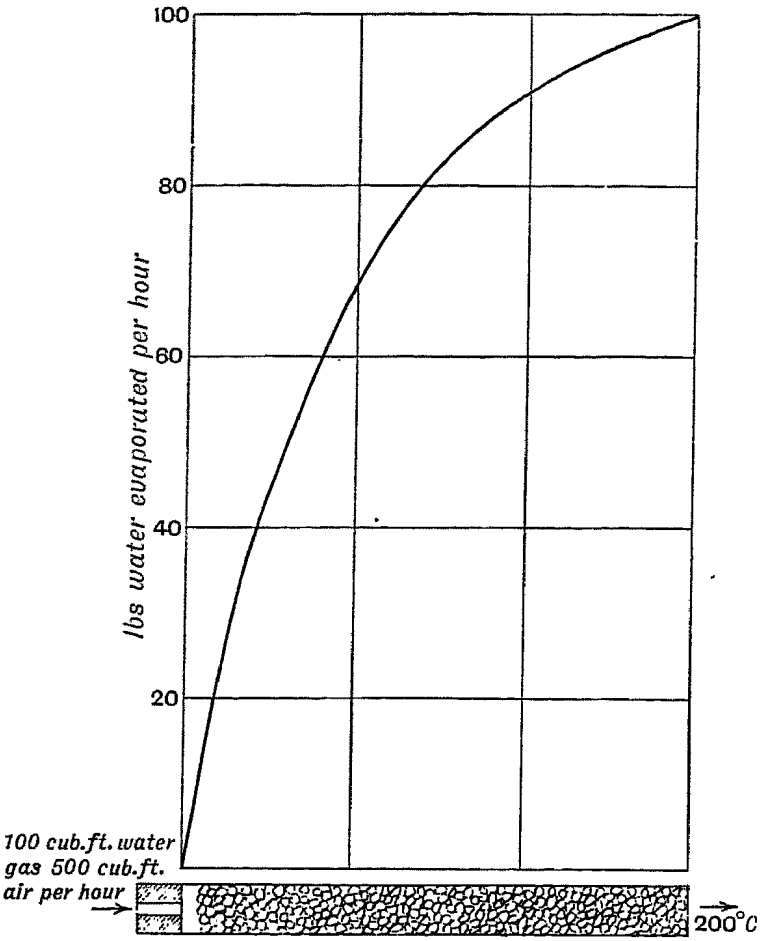
The following figures indicate the remarkable efficiency obtained when steam is raised by a gaseous fuel when this system of surface combustion is utilised:

Utilising a tube 3 feet long and 3 inches in internal diameter packed with granular refractory material as a heating unit, nearly 100 lbs. of water could be evaporated per hour (20 to 22 lbs. per square foot of heating surface) with 100 cubic feet of coal gas and 550 cubic feet of air, representing an 88 per cent transmission (to the water) of the net heat developed by the combustion (Fig. 12). This unit compared extremely favourably with the 50 per cent obtained with blast-furnace gas and the 65-70 per cent obtained with coke-oven gas when the usual gas-firing systems are employed. It was noted that the effluent gas temperature was only 200°, and in later experiments even this small amount of heat originally lost was utilised to heat up the boiler feed-water. Even better results were obtained with a large boiler erected at the Skinningrove Iron Works. This boiler, fitted with 110 heating units of the above-mentioned size, was capable of evaporating 5000 lbs. of water per hour with an average figure of 14·1 lbs. per square foot of heating surface per hour, and on a ten-hour run gave the remarkably high figure of 92·7 per cent efficiency. The efficiency of this boiler may be judged by the following figures:

Heat utilised	92·7 per cent
Heat lost in burnt gases . . .	3·0 ,,
Heat lost by radiation . . .	4·3 ,,
	100·0

Steam equivalent of power consumed by fan for driving the gases, ·7 per cent. Net overall efficiency, 90·0 per cent.

More recent improvements in the "Bonecourt" boilers include a rigid system of refractory surfaces instead of a packing of granular material for dealing with gases liable to contain dust or tar fog, and an increase in the size of the heating unit. Experimental trials[1] have shown that heating units up to 6 inches in diameter and from 13 to 21



3 ft. unit heater for boiler, showing evaporation in lbs per foot

FIG. 12.

feet long can be constructed without affecting the high rate of evaporation per square foot of heating surface.

THE INCANDESCENT MANTLE

The historical development of the incandescent gas mantle may be said to have commenced with the investigations of Drummond on the production of incandescent surfaces on certain refractories such as magnesia, lime, alumina, and zinc oxide by means of the oxy-hydrogen

[1] Bone, *Coal and its Scientific Uses* (Longmans, 1918).

flame, whilst Berzelius first pointed out the uses of thoria and zirconia as light-emitting refractories. From 1839 to 1880 several inventors were exercising their ingenuity in the production of light from the Bunsen burner flame, amongst whom may be mentioned Cruickshank in 1839, Tessié du Motay in 1867, and Edison in 1878. It was not, however, until the period 1881–83 that Williams, in New Jersey, and Auer von Welsbach, in Vienna, practically simultaneously developed what is essentially the gas mantle of to-day.

The earlier mantles were made of cotton and possessed grave defects, such as shrinkage with use, resulting in crumbling; a twist in the fibre, introduced in the spinning, making the mantle susceptible to shock, and, finally, a continuous diminution in light emissivity.

Present-day mantles are generally made of artificial silk or grass cloth (ramie fibre) spun into threads.

It may be noted in passing that all varieties of artificial silk appear suitable for the manufacture of mantle material, including the silk from Swann and Chardonnet's collodion process, the more recent Cross and Bevan viscose and acetate methods, and Schweitzer's cupro-ammonium solvent.

Auer von Welsbach commenced his researches on the fractional crystallisation of the rarer elements in 1880, and during that year he noted that cotton threads could be impregnated so as to leave a coherent oxide ash as a skeleton. The colour of the flame produced on heating this skeleton in a Bunsen burner varied from yellow to green. In 1883 the earliest mantles were introduced, in which the oxides of zirconium and lanthanum were chiefly used, although the addition of smaller quantities of other oxides was simultaneously suggested.

In 1886 the use of thoria was patented,[1] and the idea of strengthening the finished mantle for transport by immersion in collodion was also claimed.

None of these methods, however, proved satisfactory as far as life and light emissivity were concerned, these being the two most important factors for technical success. From 1886 to 1891 Welsbach and his assistant Harbinger continued unsuccessfully their experiments upon the mantle, until an accidental observation that small quantities of ceria were always present in some specimens of thoria which possessed a somewhat higher emissivity than others led to the introduction of the present-day Welsbach mantle.

The extraordinary effect that small quantities of ceria may exert on the emissivity of thoria is indicated in the accompanying curve (Fig. 13). It will be noted that the maximum emissivity is obtained when a 99·1 per cent thoria–0·9 per cent ceria mixture is utilised.[2]

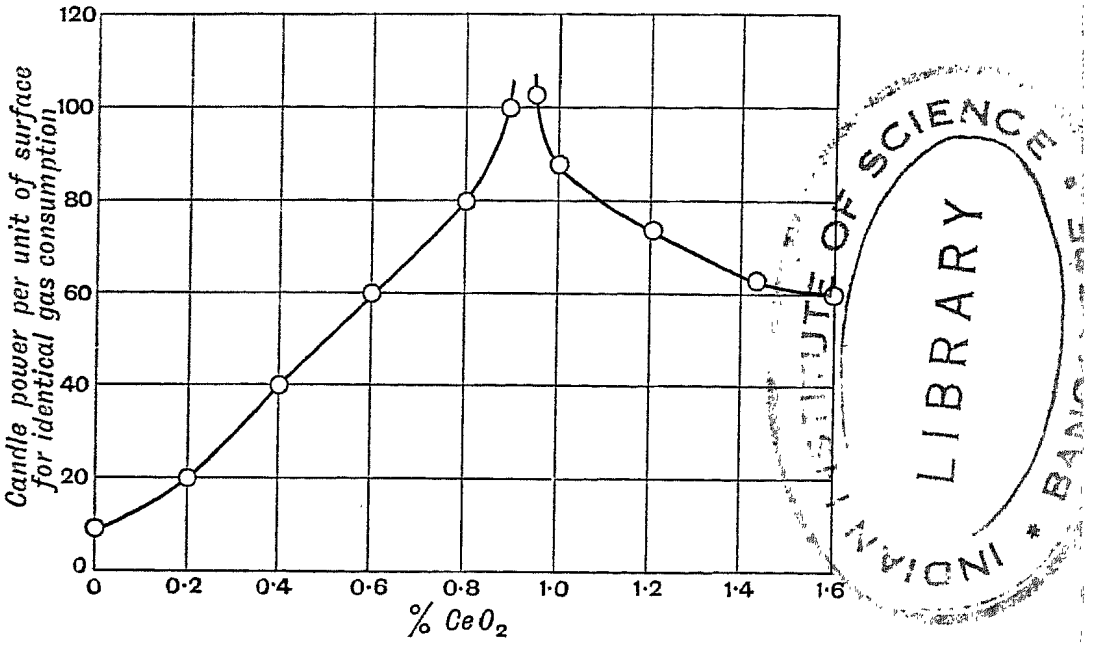
Various theories have been put forward to explain the phenomenal

[1] D.R.P. 41945.

[2] For a technical description of the manufacture of gas mantles, see R. Böhm, *Die Fabrikation der Gluhkörper für Gasglühlicht.*

increase in light emissivity in presence of ceria, but no satisfactory conclusion as to actual mechanism of light production has as yet been arrived at.

Westphal's theory that during the period of optimum emissivity the gradual combination of an acid oxide, *e.g.* thoria, with a basic one such as ceria is taking place may be dismissed as untenable. Bunte's view is supported by a certain amount of experimental evidence. He regards the thoria as a heat-insulating surface and holds that the ceria catalytically hastens the combustion of the gas-air mixture; by this means the surface of the thoria is heated up to the temperature of the flame, viz. 1700° to 1870°, and radiates at this temperature. Rubens [1] has shown that a black body radiation temperature of at least 1600°



INDIAN INSTITUTE OF SCIENCE LIBRARY BANGALORE

FIG. 13.

would be necessary to produce a similar visible emissivity. It is, however, not clear why only 0·9 to 1 per cent of ceria exerts the maximum catalytic activity. Le Chatelier was of the opinion that thoria-ceria mixtures do not radiate as "Black body" radiators, but exert selective emissivity in the region of the visible rays. Bunte, however, has shown that the emissivities of ceria and thoria and the Welsbach mantle material when heated in a muffle to the same temperatures were not sensibly different.

Wyrouboff and V. B. Lewis attributed the increased luminosity to the alternate oxidation and reduction of the ceria:

$$O_2 + 2Ce_2O_3 \rightleftarrows 4CeO_2,$$

the presence of 1 per cent of ceria in the mixture being sufficient to ensure that combustion proceeds at its maximum velocity.

[1] *Ann. Physik*, 1906, **20**, 543.

An important observation was made by Meyer and Anschütz,[1] who noted that CeO_2 forms a solid solution in thoria up to 7 per cent and that a small quantity of CeO_3 was also present in a used mantle mixture. It is an interesting speculation as to whether the maximum dissociation of the cerium oxide in the thoria occurs in dilutions 0·9 to 1 per cent.

The loss of light emissivity with continued use is attributed by White and Müller [2] to the gradual volatilisation of the catalytic cerium oxide. Bruno,[3] on the other hand, considered that the cerium oxide became converted into an inert allotropic modification from which the active oxide could be regenerated by slowly cooling the mantle.

The investigations of Swan [4] on the catalytic effect of thoria-ceria mixtures on the combustion of electrolytic gas mixtures make it appear highly probable (see p. 103) that the ceria is in fact an oxygen-carrying promoter to the catalytic thoria.

As catalytic oxygen carriers, chromium, vanadium, manganese, iron, cobalt, and even silver oxides have been suggested. With the exception of the three first-named, these oxides are much too volatile for practical use, unless retained on the mantle in the form of silicates, in which case their catalytic properties are considerably impaired. A composition of alumina and 8-16 parts of chromium oxide was largely used in the preparation of "Sunlight" mantles. With a thoria base, the following quantities of catalytic material are said to give roughly the same emissivity :

CeO_2, 0·9-1·0 ; V_2O_5, 0·4 ; MnO_2, 1·5 ; U_3O_8, 0·25 per cent.

Other bases, in addition to thoria and alumina, have been suggested from time to time, such as zirconia, magnesia, and lanthana-chalk mixtures. Magnesia has been shown to be rather volatile, whilst chalk suffers from the disadvantages of being readily attacked by water and carbon dioxide present in the air when the mantle is not in use.

Small quantities of the oxides of beryllium and aluminium are frequently added as hardeners in order to increase the resistant powers of the mantle.

The Preparation of Formaldehyde

The earliest development of the formaldehyde industry was closely associated with its utilisation as a volatile disinfectant for rooms ; for this purpose so-called formaldehyde lamps were introduced, in which methyl alcohol was caused to burn in specially constructed burners. A small fraction of the methyl alcohol was in this way converted into formaldehyde, but by far the greater portion was oxidised to carbon dioxide and steam, according to the equations

$$2CH_3 . OH + O_2 = 2H . CHO + 2H_2O,$$
$$2CH_3 . OH + 3O_2 = 2CO_2 + 4H_2O.$$

[1] *Ber.*, 1907, **40**, 2639.
[2] *J. Gas Lighting*, 1903, **83**, 504.
[3] *Zeitsch. f. Beleucht.*, 1899, **5**, 244.
[4] *J. Chem. Soc.*, 1924, **125**, 780.

Modern room disinfection by means of formaldehyde is usually accomplished by the volatilisation of paraform $(H.CHO)_3$ (Schering's formalin) in small lamps, or by chemical oxidation of methyl alcohol, by the use of permanganate [1] or barium peroxide (bleaching powder has also been suggested, Eischengrun's Autan method).

The earlier alcohol combustion lamps devised by Tollens, Bartel, Robinson, Trillat, Broche, Dieudonné, and others are no longer in use.

As new industrial uses for formaldehyde were found, notably in the hardening of gelatins, preservation of food, disinfection of hides in certain leather-tanning processes, as well as in the recent development of synthetic tannins, phenol formaldehyde condensation products for electrical insulator and other purposes (baekelite), and the fine organic chemical industry, the most suitable method of production on a technical scale became a matter of importance.

At the present time it may be stated that the only technical processes for the preparation of formaldehyde are those based on the fractional combustion of methyl alcohol; but, as will be subsequently shown, these methods will probably be replaced by more economical catalytic processes which are still in the experimental state.

The earliest experimental work on the fractional combustion of methyl alcohol to formaldehyde dates from the time of Hofmann,[2] who obtained a small conversion by the passage of an air-alcohol mixture through a red-hot platinum tube. Gautier, as well as Tollens and Loew,[3] effected certain modifications by substituting a glass tube packed with platinum or metallic copper foil as catalytic material; they laid stress on the influence of the presence of moisture in the original alcohol, the variability of yield with alteration in the oxygen-alcohol ratio, and changes in the temperature of the catalyst. Trillat,[4] in 1889, first proposed a large-scale production plant in which crude methyl alcohol was evaporated, mixed with air, and passed through the catalyst chamber containing platinum asbestos maintained at a dull red heat. Other catalytic materials, such as copper oxide or even fire-brick, were suggested. As a result of a series of experiments, Trillat was able to oxidise methyl alcohol with air by means of an electrically heated platinum gauze at 200°; with elevation of the temperature, decomposition proceeds further, as shown by the increase in the carbon monoxide and dioxide content. The optimum steam content for the methyl-alcohol vapour was found to be in the neighbourhood of 20 per cent.

With oxidised copper gauze at 330°, Trillat obtained a 48·5 per cent yield with an air-alcohol ratio of 2·5 litres to 0·65 grm. In modern practice much higher temperatures are usually attained, *e.g.* 450°-550°.

[1] Evans and Russell; see Croner, *Disinfecktion*, xi., 1909. [2] *Ber.*, 1878, **11**, 1685.
[3] *Ibid.*, 1881, **14**, 2134; 1882, **15**, 1629, **20**, 141; cf. *J. pr. Chem.*, 1886 (ii.), **33**, 321.
[4] *Oxidation des alcohols*, 1901.

Later, Sabatier and Mailhe [1] directed attention to Berthelot's experiments, in which he showed that the thermal decomposition of primary alcohols in the absence of air was effected by two simultaneous reactions :

(*a*) A dehydration, *e.g.* $C_2H_5 . OH \rightleftarrows CH_2=CH_2+H_2O$,

(*b*) A dehydrogenation, $C_2H_5 . OH \rightleftarrows CH_3 . CHO+H_2$,

and proceeded to investigate the effect of various catalytic materials on these decompositions and showed that copper at a temperature of 200°-300° was an effective dehydrogenation catalyst.

With freshly reduced copper oxide, the reduction proceeds according to the equation

$$CH_3 . OH \rightleftarrows H . CHO+H_2,$$

and the reaction is a reversible one: a 50 per cent conversion is obtained with a 5 per cent loss of decomposition products and 45 per cent unchanged methyl alcohol, which can be fractionated off and returned to the alcohol storage reservoir.

Unfortunately, in the case of methyl alcohol, copper appears rapidly to lose its activity, either owing to the gradual reduction of unchanged cuprous oxide in solid solution in the metal, which may be the real effective catalytic agent, or for some other cause as yet unknown. Consequently, experimenters have had recourse to elevation of the temperature to enhance the diminishing activity. At 300° the second stage of the thermal decomposition into carbon monoxide and hydrogen is quite marked, whilst at 350° it is practically complete in presence of metallic copper at low space velocities :

$$H . CHO=CO+H_2$$
$$\text{and } CH_3 . OH=CO+2H_2.$$

The second reaction is reversible and has been made use of for the synthesis of methyl alcohol from water gas (see pp. 257, 258). Sabatier and Senderens [2] investigated the catalytic activity of other metals and oxides on the dehydrogenation of methyl alcohol with the following results :

Substance.	Temperature Commencement of Dehydrogenation.	Temperature of Maximum Activity.	Loss of Formaldehyde due to Secondary Decomposition.
Nickel . .	180°	360°	Above 60 per cent.
Cobalt . .	Slightly more active than nickel, but less than copper.		—
Iron . . .	Slightly less active than cobalt.		—
Platinum . .	250°	—	Complete.
Manganese oxide .	320	360°	Small.
SnO_2 . . .	260	350	Small, but reduction to metal takes place.
CdO . . .	250	300	Complete.

[1] See *La Catalyse en chimie organique* and *Ann. Chim. Phys.*, 1910, **20**, 344.
[2] *Ann. Chim. Phys.*, 1905, **8**, 4473.

The following catalytic oxides suitable for dehydrogenation of methyl alcohol in order of increasing activity are cited by Sabatier. The optimum temperature for dehydrogenation appears to be 350° :

$$GlO,\ SiO_2,\ TiO_2,\ ZnO,\ ZrO_2,\ MnO,\ Al_2O_3.$$

The use of bauxite for this purpose might possess certain advantages.

It was therefore evident that the usual process of fractional combustion of methyl alcohol was actually based on the primary catalytic dehydrogenation of the alcohol into aldehyde and hydrogen, whilst the addition of oxygen might be regarded as necessary to maintain the temperature of the reaction (28 cals. being absorbed per grm.-mol. in the dehydrogenation process), to lower the partial pressure of the hydrogen, and possibly to revivify the copper catalytic material by continuous alternate oxidation and reduction. E. I. Orloff [1] confirmed nearly all Sabatier's experiments, showing that the following catalysts were effective in the dehydrogenation process. Copper precipitated on asbestos, cerium sulphate, and thorium oxide, platinum black, metallic platinum, coke containing precipitated copper, vanadium oxide on asbestos. Unsatisfactory results were obtained with iron, practically complete decomposition to oxides of carbon and lamp-black occurring.

In his later communications Orloff advises the addition of air and recommends copper gauze preceded by platinised pumice or platinised asbestos, and states that the best conversion is effected when the reaction proceeds without the application of external energy and that the following relationships are obtained :

Ratio :

O_2 : MeOH . . . . . : 0·4 : 1

Alcohol : Total volume gaseous mixture . . . : 0·342 : 1

$$\frac{\text{Concentration of oxygen} \times \text{concentration of alcohol vapour}}{\text{Square of mean velocity of gas flow}} = 0{\cdot}00103.$$

Le Blanc and E. Plaschke [2] similarly conducted a series of experiments on fractional combustion of methyl alcohol, using silver wire gauze and electrolytically silvered copper gauze as catalysts ; they also arrived at the conclusion that the process is virtually one of dehydrogenation and that the function of the oxygen was merely to revivify the catalytic material, for which purpose freshly reduced copper was most suitable. Their most favourable yields were 58 per cent with silver and 55·4 per cent with copper, under the following experimental conditions :

[1] *J. Russ. Phys. Chem. Soc.*, 1907, **39**, 855, 1023, 1414 ; 1908, **40**, 796.
[2] *Zeitsch. Elektrochem.*, 1911, **17**, 151.

Length of Silver Gauze Spiral in cm.	Grm. O_2 per grm. Alcohol.	Temp. of Catalyst.	Velocity of Air in litres per minute.
5·85	0·459	455°	2·669*

Per cent Conversion.	Per cent Unchanged.	Per cent Loss.	Diameter of Tube.
58·06	26·43	15·51	30 mm.

* Representing a space velocity referred to the air of 3900 (litres of air per litre of catalyst space per hour).

The effluent gas contained the following proportions of CO_2, CO, and H_2 respectively: 4·46, 4·16, and 11·49 per cent.

The figures represent the optimum yield obtained after alteration of all the independent variables one at a time.

Fokin [1] continued Orloff and Le Blanc's researches and obtained the following orders of activity for the conversion in the passage of alcohol-air mixtures over different metals:

Ni	1·08 per cent	Cu	43·47 per cent
Al	1·5 ,,	Ag	64·60 ,,
Mn	2·01 ,,	Au	71 ,,
Co	2·8 ,,	CuAg alloy	84 ,,
Pt	5·2 ,,		

It will be noted that silver is extremely effective.

Bouliard [2] suggests the use of silver precipitated on flax as support material, whilst O. Blank [3] suggests silver on asbestos.

Hochstetter [4] has attempted to produce a catalytic material which should accelerate both reactions, viz. the dehydrogenation process, $CH_3 . OH = H . CHO + H_2$, as well as the fractional combustion, $2CH_3 . OH + O_2 = H . CHO + H_2O$. Thus, he states that he has obtained the following results by using metal couples instead of the pure metals:

	Per cent Yield.
Pure Cu	70
Cu alloyed with 1/10,000 Pt	72
Cu coated with 1/10,000 Pt	77
Ag	75
Ag with a Cu tube	84
Ag coated with 1/10,000 rhodium	96
Ag ,, ,, 1/10,000 Pt	96

Other suggested methods of preparation of formaldehyde have been the subject of patent literature.

Both the Badische [5] and Dreyfus [6] patents suggest passing a mixture of carbon monoxide and hydrogen in the ratio of 2 : 1 at 100 atmospheres pressure over catalytic materials (such as Pt, Cu, Fe, Cr, Ni, Ce, Ur, V, or their oxides) at 300°-400°. (See further, pp. 257, 258.)

Brodie,[7] Losanitsch, and Jovitschitsch [8] obtained small quantities of formaldehyde from these gases when subjected to the silent electric

[1] *J. Russ. Phys. Chem. Soc.*, 1913, **45**, 286.
[2] F.P. 412501/1910.
[3] *J. Soc. Chem. Ind.*, 1911, **30**, 49.
[4] B.P. 464/1914.
[5] B.P. 20486/1913.
[6] B.P. 108855/1915.
[7] *Proc. Phys. Soc.*, 1874, **12**, 171.
[8] *Ber.*, 1897, **30**, 135.

discharge, Chapman and Holt [1] by the high-tension electric discharge, whilst de Jahn proved the presence of aldehyde when CO and H_2 were passed over spongy platinum into water.[2]

The thermal decomposition of dimethyl ether, tin formate,[3] and calcium formate, as well as the fractional reduction of formic acid by hydrogen over iron or nickel catalysts at 300° to 500°,[4] are all suggested methods for the preparation of formaldehyde.

Equally interesting and worth attention are the various suggestions for the fractional combustion of methane into methyl alcohol or formaldehyde.

Glock,[5] in 1898, suggested the passage of a mixture of methane and air over granulated copper or pumice maintained at 800°, the process, being circulatory, removing the formaldehyde after each cycle by a system of scrubbers. Lance and Elsworthy [6] suggest the use of hydrogen peroxide or persulphuric acid as an oxidant in the presence of ferrous sulphate, presumably as a catalytic material. The Sauerstoff u. Stickstoff Ind.[7] and V. Unruh [8] claim the use of tan bark as catalyst, stating that oxidation of methane by air will take place at 30°-50° in the presence of such material. It is more than probable that the aldehyde was itself derived from the tan bark under the conditions of operation. Fernekes [9] describes a special combustion furnace for the fractional oxidation of methane, whilst Otto [10] suggests the use of ozone as an oxidant. Lacy [11] describes the direct chemical conversion process, $CH_4 \longrightarrow CH_3Cl \longrightarrow CH_3 . OH$, whilst Lance and Elsworthy [12] claim the production of methylamine by hydrogenation of hydrocyanic acid over a metal catalyst with subsequent decomposition of the amine with steam in the presence of a catalyst:

$$CH_3 . NH_2 + H_2O \longrightarrow CH_3 . OH + NH_3.$$

Bone and Wheeler showed that a 20 per cent yield could be obtained by the flameless combustion of methane on borosilicate glass beads.

The fractional oxidation of other alcohols can be accomplished in like manner. Thus, glycerine in the presence of air will give small quantities of glycerine aldehyde in the presence of platinum black, ethyl alcohol and air passed over platinised pumice at a dull red heat yields 16·8 per cent of acetaldehyde, eugenol in a similar manner yields 2·9 per cent of vanillin. It will, however, be noted that the yield of aldehyde is invariably small when the process of fractional combustion is adopted, whilst the catalytic dehydrogenation processes, on the other hand, usually give good yields with very small losses.

The partial oxidation of hydrocarbons.—In view of the technical importance of the conversion of the hydrocarbons, both aromatic and

[1] *J. Chem. Soc.*, 1905, **87**, 916.
[2] *Ber.*, 1889, **22**, 989.
[3] B.P. 183856.
[4] Badische Co. Pat. 185932.
[5] D.R.P. 107014. See also D.R.P. 286731.
[6] B.P. 7297/1916.
[7] D.R.P. 214155/1906.
[8] U.S.P. 891753/1907.
[9] U.S.P. 1038546/1912.
[10] *Ann. Chim. Phys.*, 1898 (vii.), **13**, 77.
[11] B.P. 16194/1914.
[12] B.P. 4409/1906.

aliphatic, into the more valuable oxidation products, numerous attempts have been made to effect such partial oxidation with air as oxidising agent in the presence of various catalytic agents.

These methods naturally divide themselves into those in which liquid phase and those in which vapour phase oxidation is made use of. Although in catalytic hydrogenation both liquid and vapour phase catalytic reduction have proved successful, in catalytic oxidation only the latter has been developed to the technical stage.

In the case of hydrocarbons of the aromatic series Wedge [1] claimed the liquid phase oxidation of benzene to phenol, utilising platinum black as catalytic agent, whilst Willstätter and Sonnenfeld [2] describe the use of platinum as a catalyst in the fractional oxidation of cyclohexanol to adipic acid. More attention has been paid to the liquid phase fractional oxidation of the long chain aliphatic hydrocarbons with a view to the production of synthetic fats. Grün [3] and Fischer and Schneider [4] have noted that oxidation proceeds slowly at the melting point of the wax, the reaction velocity increasing with rise in temperature. An upper limit of *circa* 150° C. is set to the temperature so as to avoid as far as possible the degradation of the long chain aldehydes, alcohols, and acids produced by further oxidation. A 50 per cent yield of odd-numbered chain fatty acids may be obtained by low-temperature oxidation of several months' duration. The reaction appears to be somewhat complicated, since the formation of unsaturated oxy-derivatives always occurs, and the course of the oxidation can in fact be followed by the determination of the iodine value. The reaction is slightly autocatalytic in action, since the seeding of a fresh wax with a partially oxidised fraction accelerates the oxidation, at least in the primary stages.

Many attempts have been made to accelerate this low-temperature oxidation process by the addition of catalysts, notably by alkalis and various oxygen carriers such as salts of iron and manganese. The results, however, appear to be inconclusive.

More successful have been the processes of fractional oxidation of volatile hydrocarbons in the vapour phase. We have already referred to the production of formaldehyde by the partial oxidation of methane. Sabatier and Mailhe [5] have shown that small quantities of aldehydes and alcohols can be produced by the catalytic combustion of paraffinoid hydrocarbons, whilst similar results were obtained by Orloff [6] utilising copper oxide gauze as catalytic agent. The first attempts to oxidise aromatic hydrocarbons catalytically were made by Coquillon,[7] who noted the production of both benzaldehyde and benzoic acid on the passage of either benzene or toluene vapour and air over an incandescent platinum wire. Walter showed [8] that benzoic acid and benzaldehyde

[1] B.P. 2010/1901. [2] *Ber.*, 1913, **46**, 2952. [3] *Ibid.*, 1920, **53**, 987.
[4] *Ibid.*, 1920, **53**, 922. [5] *Compt. rend.*, 1906, **142**, 1394.
[6] *J. Russ. Phys. Chem.*, 1907, **39**, 855, 1023; 1908, **40**, 1414.
[7] *Compt. rend.*, 1875, **80**, 1089. [8] *J. pr. Chem.*, 1892, **107**, 111.

would readily be produced by the fractional oxidation of toluene and anthraquinone from anthracene, utilising vanadium pentoxide as catalytic agent.[1] Coke [2] and chromium oxide [3] have been suggested for similar purposes. Weiss and Downs [4] have investigated in detail the conditions for the fractional oxidation of naphthalene to phthalic anhydride and the formation of maleic anhydride from benzene. It is interesting to note that small quantities both of phenol (0·3 per cent) and benzoquinone were obtained from benzene. In the presence of steam and at high pressures diphenyl was likewise obtained in moderate amount. The most effective catalyst was found to be vanadium pentoxide.[5]

The difficulties successfully overcome by Weiss and Downs are those inherent in such processes of oxidation of organic substances, namely, those of temperature control. These are apparent from the following data on the thermal values of three typical catalytic gaseous oxidation processes:

Reaction.	Optimum Temperature of Catalysis.	Optimum Air Reactant Ratio by Volume.	Heat developed. B.T.U. per lb. of Reactant.	Heat Capacity of entering Gases at 25° C. at Optimum.
$SO_2 \longrightarrow SO_3$.	400° C.	7·5 : 1	635	661
$NH_3 \longrightarrow NO$.	750° C.	10 : 1	5,660	6260
$C_6H_6 \longrightarrow$ Maleic anhydride .	400° C.	22·5 : 1	10,560	1620

It will be observed that provision has to be made for the dissipation of heat sixteen times greater than that evolved in the oxidation of sulphur dioxide, and that in addition local elevation of temperature has to be avoided, as the reactions of fractional oxidation are not reversible as is the case in the sulphur dioxide-trioxide equilibrium.

Oxidation at charcoal surfaces.—In view of the biological importance of low-temperature surface combustion many experiments have been made with charcoal as a catalyst for the oxidation of organic materials.

The results of numerous investigations on the adsorption of oxygen by charcoal, notably by Baker,[6] Dewar,[7] Rhead and Wheeler,[8] indicate that oxygen may be adsorbed on a charcoal surface to form at least three types of surface compounds which may be associated with the diamond, paraffin, and ethenoid portions of the surface. One form is removable only at high temperatures as oxides of carbon, another removable as oxides of carbon by evacuation or by fusion with sodium carbonate,[9] and a third which can, under certain conditions, be recovered as oxygen. This last form is endowed with catalytic properties, for

[1] See also D.R.P. 168291/1904; F.P. 360785/1905; and B.P. 21941/1905.
[2] Woog, *Compt. rend.*, 1907, **145**, 174.
[3] Lowenthal, D.R.P. 239651/1909.
[4] U.S.P. 1318631, 2, and 3/1919.
[5] *J. Ind. Eng. Chem.*, 1920, **12**, 228.
[6] *J. Chem. Soc.*, 1889, **51**, 249.
[7] *Compt. rend.*, 1904, **139**, 201.
[8] *J. Chem. Soc.*, 1913, **103**, 461, 1210.
[9] Taylor, *J. Amer. Chem. Soc.*, 1921, **43**, 2059.

not only does low-temperature autoxidation occur but many processes of oxidation are catalytically accelerated. Calvert [1] noted the oxidation of ethyl-alcohol vapour and gaseous hydrocarbons, a result confirmed by Firth.[2] Feigel [3] noted the catalytic oxidation of solutions of sulphides, chromates, and iodides. Warburg and his co-workers have examined the catalytic oxidation of oxalic and certain α amino acids;[4] Meyerhof the oxidation of glucose in the presence of phosphoric acid;[5] Freundlich and Bjerke [6] the oxidation of phenylthio-carbamide, and Rideal and Wright [7] that of malonic acid.

The autoxidation process is found to be of zero order and independent of the oxygen pressure over a considerable range at high pressures, with a temperature coefficient of $\frac{K_{50}}{K_{40}} = 1{\cdot}80$. By selective poisoning Rideal and Wright found that with an active sugar charcoal of mean surface area of 266 cm.^{2} per milligrm. only 0·38 per cent of the surface was autoxidisable.

The oxidation of acids such as oxalic acid proceeds over a relatively much greater area: thus, for the particular form of charcoal, viz. sugar charcoal, the fraction catalytically active in effecting the oxidation of oxalic acid was found to be 40·5 per cent. Both acid and oxygen are adsorbed, the reaction velocity rising to a maximum and falling again as the concentration of oxalic acid is increased. The optimum velocities were obtained at a concentration of 0·0075 molar oxalic acid and 0·050 molar malonic acid, with a temperature coefficient of $\frac{K_{50}}{K_{40}} = 2{\cdot}0$.

The reaction velocity as a function of the concentration of the reactants was found to be expressible in the form

$$\frac{\partial x}{\partial t} = \frac{K\sqrt{P_{O_2}}C_{ox}}{(1 + m\sqrt{P_{O_2}} + nC_{ox})^2},$$

which reduces to the simpler forms

$$\frac{\partial x}{\partial t} = K' C_{ox} / \sqrt{P_{O_2}}$$

for small oxalic concentrations, and to

$$\frac{\partial x}{\partial t} = K'' \frac{\sqrt{P_{O_2}}}{C_{ox}}$$

for high concentrations of acid, both being experimentally realised for a number of such surface oxidations.

Such charcoals can readily be activated or promoted by heat treatment with urea and iron salts or dye-stuffs and iron salts.

[1] *J. Chem. Soc.*, 1867, **20**, 293.
[2] *Trans. Farad. Soc.*, 1924, **20**, 370.
[3] *Zeitsch. anorg. Chem.*, 1921, **119**, 305.
[4] *Pflüger's Archiv*, 1914, **155**, 547; *Biochem. Zeitsch.*, 1921, **113**, 257; 1924, **145**, 461.
[5] *Biochem. Zeitsch.*, 1923, **135**, 558.
[6] *Zeitsch. physiol. Chem.*, 1916, **91**, 31.
[7] *J. Chem. Soc.*, 1925, **127**, 1347.

It is found that this treatment brings about two distinct changes in the surface; firstly, a general extension, of which a large portion possesses approximately the same specific catalytic activity as the original charcoal. In addition a small portion, only some 2·0 per cent, of the surface is extremely active, and owing to the sensitivity of these portions to poisoning by potassium cyanide it is probable that these portions are the true promoted iron charcoal systems.

These reactions afford an excellent example of the two effects of promoters discussed in Chapter III.

The Preparation of Acids

The further oxidation of the aldehydes into the corresponding acids by a catalytic process has been successfully developed in the case of acetaldehyde; as catalyst, manganese acetate, or more rarely the formate, butyrate, lactate, or benzoate, dissolved in acetic acid is employed in the proportion of 300 kilos. of aldehyde to 3 kilos. of manganese acetate. Aeration is accomplished under pressure, and the aldehyde is converted practically quantitatively into acetic acid. Several difficulties were associated with the earlier phases of the process. The reaction is strongly exothermic, and a very efficient cooling system has to be employed; at the same time a sufficient depth of liquid to ensure proper aeration must be maintained. All metals sufficiently robust to stand the pressures employed are rapidly attacked under the combined influence of oxygen and acetic acid, thus entailing a heavy repair bill. Pure aluminium liners are frequently employed. The most serious difficulty is the danger of explosion associated with the formation of the extremely unstable peracetic acid, $CH_3 . CO . OOH$, under continued aeration in the presence of the manganese salt; over-aeration has thus to be carefully avoided. Grunstein and Behrens have shown that other catalytic substances, such as the oxides of vanadium, uranium, cerium, and iron, possess an activity equal to that of the manganese salts,[1] but that their use is attended with a greater risk of explosion, since these salts are not specially active in the removal of the peracetic acid by reduction with aldehyde, according to the equation

$$CH_3 . CO . OOH + CH_3 . CHO = 2CH_3 . COOH,$$

a reaction which is accelerated by manganese. In technical working a 30 per cent loss occurs, due to further oxidation of the acetic acid to carbon dioxide and water.

Ethyl alcohol can be directly oxidised to acetic acid by admixture in the vapour state with air and passage over platinum black or vanadium pentoxide.

The preparation of oxalic acid by the oxidation of sugar and starches

[1] *Compt. rend.*, 1907, **145**, 124.

is no longer accomplished by means of hot nitric acid, which entails a ve considerable loss in the form of carbonate, tartaric, mucic, and saccha acids, but use is made of the observation[1] of Naumann, Moeser, a Lindenbaum that the addition of 0·2 per cent of vanadic oxide effects t conversion almost quantitatively in the cold in from ten to twenty hou

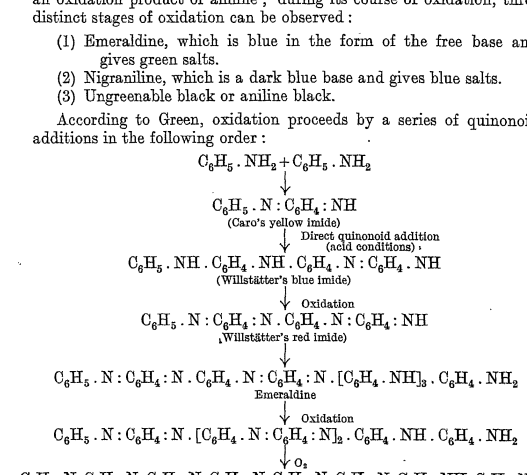
The Use of Catalytic Oxidation Processes in the Dye Industry

Aniline black.—The preparation of aniline black, one of the mo important dyes for cotton yarns, was first developed by John Lightfoo of Accrington, in 1863, and is now largely employed in all the dyei industries.

The constitution of the dye was proved by A. G. Green,[2] w contributed a very important addition to the number of catalyt oxidation processes of technical importance. Aniline black is essential an oxidation product of aniline; during its course of oxidation, thr distinct stages of oxidation can be observed:

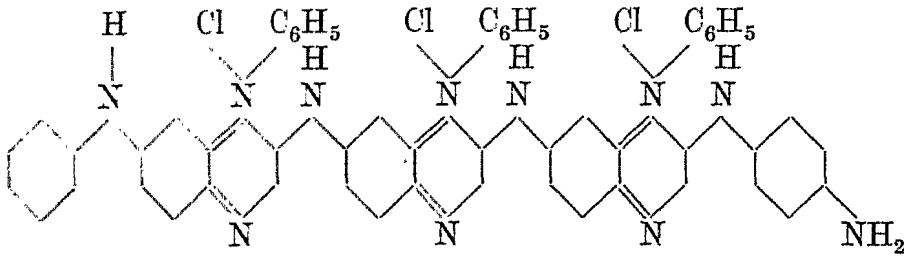
(1) Emeraldine, which is blue in the form of the free base a gives green salts.
(2) Nigraniline, which is a dark blue base and gives blue salts.
(3) Ungreenable black or aniline black.

According to Green, oxidation proceeds by a series of quinoi additions in the following order:



[1] B.P. 17424/1911.

[2] *J. pr. Chem.* (ii.), 1907, **75**, 146.



Aniline black.

The usual oxidising agents employed are bichromates or sodium chlorate, whilst copper sulphate, copper sulphide (prepared by the double decomposition of copper sulphate and sodium sulphide), or vanadium chloride are used as catalysts.

For example, a 15 per cent aniline hydrochloride solution (neutralised with free base), with 5 per cent of sodium chlorate as oxidising agent, is mixed with 5 per cent of a 54 per cent copper sulphide paste to form an effective dyeing-bath. The quantity of vanadium salt required to exert the same catalytic activity as the copper salts normally employed is far less. Sabatier [1] states that only 1 part in 70,000 parts of aniline is required; Witz estimates the ratio at 1 : 270,000, whilst the following is the composition of a dye-bath actually employed.

Parts by weight:

8 per cent aniline hydrochloride.
1·5 per cent aniline.
4 per cent sodium chlorate.
5 per cent vanadium salt solution.

The solution of the catalytic material is made as follows: 8 grms. of ammonium vanadate are dissolved in 40 grms. of 30 per cent hydrochloric acid and 80 c.c. of water. Ten grms. of glycerin are added, and the whole is made up to 2 litres. The ratio aniline salt to vanadium salt is approximately 47,500 : 1. This dyeing-bath is, it is stated, not so good as the copper sulphide catalyst bath, since it is rather too rapid in operation, and part of the dye is deposited in the solution itself or loosely adherent to the fibre.

Green,[2] in 1907, made the interesting discovery that bichromate and chlorates could be replaced by air as oxidising agent provided that certain promoters were added to the catalytic agents usually employed. In this way a considerable economy in materials was effected, and all tendering of the fibre occasioning weakening due to the formation of the oxycelluloses was avoided.

As promoters, small quantities of a *p*-diamine or *p*-amidophenol were found most effective. The use of amidophenol, *p*-phenylenediamine and its sulphonic and carboxylic derivatives, dimethyl-*p*-phenylenediamine, *p*-amidophenylaniline, benzidine, diamidodiphenyl-

[1] *La Catalyse.* [2] B.P. 16189/1907.

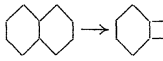
aniline, quinone, mono- and di-imides and their chlorides, *p*-nitrophenol, nitrodimethylaniline, *p*-amidophenylquinonimide and their homologues and derivatives, is claimed.

The addition of 4 per cent of the promoter on the weight of aniline taken is said to be sufficient. The mechanism of operation has not been fully explained, but the catalyst probably hastens the oxidation process by the intermediate formation of complex indamines. Iron, cerium, uranium, and osmic salts exert similar catalytic activity in this oxidation process, but have not received technical application.

Methyl-violet and fuchsine.—Cupric chloride and small quantities of phenol are frequently added in the oxidation of dimethylaniline to methyl-violet. It is said that with suitable proportions of catalyst and promoter (phenol) the oxidation can be effected with atmospheric oxygen in lieu of the sodium chlorate usually employed.

In the oxidation of aniline and *o*- and *p*-toluidine to fuchsine, nitrobenzene can be used as oxidising agent in the presence of a small quantity of a vanadium salt or slightly larger quantities of ferric chloride.

Indigo.—Heumann's synthesis of indigo, which was successfully developed by the Badische Co., was based upon the primary conversion of crude naphthalene into phthalic acid, utilising fuming sulphuric acid as an oxidant:



It may be noted in passing that the growth of the contact sulphuric-acid process in Germany was determined by the demand for fuming sulphuric acid in the production of this dye.

Groebe [1] accidentally discovered that mercury was an effective catalytic agent in this process of oxidation between 200° and 300°. Further investigation, singularly enough, proved that mercuric sulphate was one of the most effective; copper sulphate, although exerting a reasonable catalytic activity, is inferior, although a mixture of copper and mercuric sulphates is superior to either constituent used singly.[2] Nickel and iron are slightly active, whilst the salts of manganese, potassium, and magnesium are inactive.

The use of a small globule of mercury or a strip of copper in the usual Kjeldahl process of nitrogen estimation is a striking application of these catalysts to the oxidation of nitrogenous organic matter by strong sulphuric acid.

The patents of Rosenthal [3] also illustrate the oxidising action of mercury salts. The 10 per cent yield of tertiary bases of the aromatic group obtained by oxidation of tertiary aromatic amines with sulphuric acid at temperatures above 200° is increased to a 60 per cent yield in presence of mercury.

[1] *Ber.*, 1896, **29**, 2806.

[2] Bredig and Brown, *Zeitsch. physikal. Chem.*, 1903, **46**, 502.

[3] D.R.P. 127179 and 127180.

Autoxidation and Induced Oxidation

The investigations on the direct oxidation by means of oxygen gas of a number of organic substances has indicated that the process cannot take place by means of a simple addition, *e.g.*

$$2X + O_2 \longrightarrow 2XO,$$

where X is the substance undergoing oxidation to the stable oxide XO. The classic researches of Schönbein [1] indicated clearly that, in many cases of oxidation, for every molecule of oxygen consumed a molecule of oxygen was simultaneously converted into a more active state; this active oxygen could then secondarily react either with more oxygen to form ozone, with water to form hydrogen peroxide, or in the presence of other oxidisable substances could oxidise them, frequently causing oxidations which cannot be accomplished by ordinary atmospheric oxygen. For example, hydrogen peroxide is formed during the rusting of lead, zinc, and probably iron; ozone is formed during the oxidation of phosphorus. Indigo is converted into isatin during the autoxidation of palladium hydride, benzaldehyde, or turpentine. Various of the more important theories which have been advanced to explain the mechanism of these processes may be briefly classified as follows:

The dualistic theory.—Schönbein [2] was of the opinion that these cases of autoxidation were best interpreted on C. Brodie's [3] hypothesis, in which ordinary oxygen during the process of oxidation is split up into two parts, "ozone" and "antozone":

$$O_2 \begin{cases} \nearrow \bar{O}, \text{ or ozone.} \\ \searrow \overset{+}{O}, \text{ or antozone.} \end{cases}$$

R. Clausius [4] more definitely stated that Brodie's ozone and antozone could be regarded as atomic oxygen of opposite electric charges:

$$O_2 \longrightarrow \dot{O} + O'.$$

Van 't Hoff,[5] as a result of his experiments on the autoxidation of phosphorus, introduced the hypothesis that atmospheric oxygen is, already prior to any process of oxidation, normally partly dissociated into charged atomic oxygen, and that the equilibrium $O_2 \rightleftarrows \dot{O} + O'$ must be considered as an important factor in oxidation phenomena.

According to the above hypothesis, all processes of autoxidation are dual in character, two substances simultaneously undergoing oxidation. Engler [6] has attempted to distinguish between these by terming the substance undergoing oxidation the autoxidiser, and the

[1] *J. pr. Chem.*, 1858–1868, 73-99. [2] *Loc. cit.* [3] *Phil. Trans.*, 1850, **141**, 759 *et seq.*
[4] *Pogg. Ann.*, 1858, **103**, 644. [5] *Zeitsch. physikal. Chem.*, 1895, **16**, 411.
[6] *Kritische Studien über die Autoxydationsvorgänge, Braunschweig*, 1903.

substance simultaneously oxidised the acceptor. It is evident that either the autoxidiser or the acceptor may react, on the one hand, with the ozonic, or, on the other, with the antozonic form of the active oxygen, depending on the chemical nature of the substances undergoing oxidation; thus water, phosphorus, the alkali metals, and the alkaline-earth metals form antozonides on oxidation, whilst ozone and the chromates, permanganates, hypochlorites, and vanadates, as well as lead, zinc, nickel, bismuth, silver, and manganese oxides, are ozonides.

Van 't Hoff noticed that in the case of phosphorus undergoing atmospheric oxidation in the presence of indigo acting as acceptor, a continuous supply of fresh acceptor was required to maintain the velocity of oxidation up to a measurable speed. He consequently argued that the reaction $O_2 \rightleftarrows \dot{O} + O'$ must be a reversible one, since the accumulation of the ozonic form of active oxygen normally removed in the oxidation of the indigo to isatin retarded the action of the antozonic oxygen on the phosphorus.[1]

It must be admitted that a search for the charged ozonic modification of oxygen which should be present in the air after passage over phosphorus has yielded conflicting results. Elster and Geitel[2] noted that air thus treated was electrically conducting,[3] and Goekel[4] showed that this conductivity was not due to the presence of ozone, which could be absorbed without destroying the conductivity. Barus,[5] Harms,[6] and Bloch,[7] on the other hand, have shown that the conductivity cannot be attributed to the ozonic oxygen or charged ionic oxygen, but is due to oxides of phosphorus collected round charged nuclei forming aggregates of relatively large dimensions ($r = 10^{-6}$ cm.), whilst the actual number of charged ions observed fell far short of the stoichiometric ratio, oxygen absorbed : oxygen ionised = 1 : 1, postulated by the hypothesis.

E. Hoppe-Seyler[8] and Baumann adopted the same hypothesis as Schönbein, but substituted the term "nascent" oxygen for Schönbein's ozonides and antozonides; according to these investigators, processes of autoxidation may be represented by the general equation

$$X + O_2 \longrightarrow XO + \text{nascent oxygen},$$

and such nascent oxygen was to be regarded as possessing superior activity to the substance in the ordinary molecular state. It is evident that the difference in view is one of nomenclature rather than of principle.

[1] See J. Joubert, *Thèse sur la phosphorescence du phosphore*, 1874; T. Ewan, *Phil. Mag.*, 1894 (v.), **38**, 512; J. Chappuis, *Bull. Soc. chim.*, 1881 (ii.), **35**, 419.

[2] *Wied. Ann.*, 1890, **39**, 321; *Physikal. Zeitsch.*, 1903, **4**, 457.

[3] See also Mattenci, *Encyc. Brit.*, 1855, **8**, 622; Naccari, *Atti delle Scienze di Torino*, 1890, **25**, 252.

[4] *Zeitsch. physikal. Chem.*, 1903, **4**, 16.

[5] *Experiments with Ionised Air*, Washington, 1901.

[6] *Zeitsch. physikal. Chem.*, 1902, **3**, 111.

[7] *Ann. Chim. Phys.*, 1905 (viii.), **4**, 25.

[8] *Zeitsch. physiol. Chem.*, 1878, **2**, 22.

The intermediate compound theory.—M. Traube,[1] Gisammetti,[2] . Bach,[3] C. Engler and V. Wild,[4] and others developed the hypothesis f the intermediate compound.

Thus, according to M. Traube, the process of autoxidation of the ietals with the simultaneous formation of hydrogen peroxide takes lace through the presence of water as intermediary, as represented by ie equation

$$M + O:H_2 + O_2 \longrightarrow MO + H_2O_2.$$

Hydrogen peroxide is thus reduced oxygen, and not oxidised water s postulated by Schönbein and his co-workers. The curious reducing ctions of hydrogen peroxide, *e.g.*

$$Ag_2O + H_2O_2 = 2Ag + H_2O + O_2,$$

e cited to support this claim.

According to Traube, the stoichiometric ratio

$$MO : H_2O_2 :: 1 : 1$$

eed not necessarily be observed in practice, as the secondary reaction

$$M + H_2O_2 = M(OH)_2$$

ay take place. Such a reaction is extremely unlikely, and the usual screpancy between the theoretical quantity of peroxide and that ctually obtained must be put down to thermal decomposition.

The necessity for the presence of at least small quantities of water apour in processes of combustion [5] has been observed by many independent investigators, and its function as an intermediary catalyst electrolyte to complete the voltaic circuit need not be discussed at is point. The application of this principle to explain certain cases autoxidation and induced oxidation forms an important extension the hypothesis. It will be noted that the formation of substances ch as ozone, permanganate, and the oxides of the heavy metals, . Schönbein's ozonides, must be considered as secondary reactions king place between the hydrogen peroxide and the acceptor. In me cases, as, for example, in the formation of ozone from oxygen d hydrogen peroxide, or of silver oxide from hydrogen peroxide and ver, this assumes exceedingly improbable reactions.

A. Bach adopted another point of view, in which an intermediary roxide was first formed, prior to the decomposition into an oxide d with simultaneous oxidation of the acceptor. Thus, in the oxidation

[1] *Ber.*, 1882, **15**, 663; 1893, **26**, 1471. [2] *Abhandlungen*, Berlin, 1899.
[3] *Compt. rend.*, 1897, **126**, 2, 951. [4] *Ber.*, 1897, **30**, 1669.
[5] See Mrs. Fulhame, *An Essay on Combustion*, London, 1794; H. B. Dixon, *Phil. Trans.*, 4, **175**, 630; *J. Chem. Soc.*, 1886, **49**, 95; and H. E. Armstrong, *Brit. Assoc. Reports Proc.* . *Soc.*, 1886, **40**, 287.

of a metal in the presence of water, a metallic oxide and hydrogen peroxide are assumed to be formed according to the following scheme :

$$M + O_2 = M\begin{matrix}O\\O\end{matrix}$$

$$M\begin{matrix}O\\O\end{matrix} + H_2O = MO + H_2O_2.$$

In the oxidation of phosphorus with the simultaneous production of ozone we may adopt the equations of Engler and Wild,[1] or of Ostwald,[2] to explain the mechanism on Bach's intermediate peroxide theory :

$$(a)\quad 2P + O_2 = P_2O_2$$

$$P_2\begin{matrix}O\\O\end{matrix} + O_2 = P_2O + O_3,$$

$$(b)\quad 2P + 2O_2 = P_2O_4 = P_2O + O_3,$$

giving the stoichiometric ratio $P : O_2 :: 2 : 1$, the ratio actually obtained by van 't Hoff.

Bodländer,[3] and Baeyer and Villiger,[4] in researches on the oxidation by air the actor, of benzaldehyde the inductor, with indigo as an acceptor, gave additional support to Bach's theory by the isolation of an intermediary peroxide, benzoyl hydrogen peroxide :

$$C_6H_5 . CHO + O_2 = C_6H_5 . CO : O(OH),$$

which peroxide could then react in two distinct ways :

(*a*) With another molecule of benzaldehyde,

$$C_6H_5 . CO : O(OH) + C_6H_5 . CHO \longrightarrow 2C_6H_5 . COOH.$$

(*b*) With the acceptor indigo,

$$C_6H_5 . CO : O(OH) + \text{indigo} \longrightarrow C_6H_5 . COOH + \text{isatin}.$$

The hypothesis of a primary formation of an unstable peroxide of the inductor has been further strengthened by isolation of such salts in the case of cerium oxide by Job,[5] and in the case of ferric and ferrous iron by Manchot,[6] Goard and Rideal,[7] Bohnson and Robertson.[8]

It is clear that this hypothesis may be extended in the following manner. The primary reaction between inductor and oxygen to form an unstable peroxide may be represented as follows :

$$(1)\quad A + O_2 \longrightarrow AO_2.$$

[1] *Ber.*, 1897, **30**, 1669.
[2] *Zeitsch. physikal. Chem.*, 1900, **34**, 250.
[3] *Ahrens Sammlung*, 1889, **3**, 470.
[4] *Ber.*, 1900, **33**, 585, 3480.
[5] *Ann. Chim. Phys.*, 1900 (vii.), **20**, 205 ; *Compt. rend.*, 1902, **134**, 1052.
[6] *Zeitsch. anorg. Chem.*, 1901, **27**, 397 ; *Ber.*, 1901, **34**, 2479.
[7] *Proc. Roy. Soc.* (*A*), 1924, **105**, 150.
[8] *J. Phys. Chem.*, 1921, **25**, 19 ; *J. Amer. Chem. Soc.*, 1923, **45**, 2493.

The peroxide AO_2 may then react with another molecule at A,

$$(2) \quad A + AO_2 \longrightarrow 2AO,$$

a view supported by Moureu in his extensive researches on the mechanism of inhibition of these autoxidations.

Alternately the peroxide AO_2 may react with the acceptor B,

$$(3) \quad B + AO_2 \longrightarrow AO + BO,$$

to form stable oxides both of A and of B.

In some cases the oxide AO may be again reduced by B to the inductor A,

$$(4) \quad AO + B \longrightarrow A + BO.$$

In the case of reactions proceeding to the stage (3) the final result of oxidation is evidently the complete oxidation of the acceptor B to the stable oxide BO. For every molecule of B undergoing oxidation at least one molecule of A has undergone a similar process, but if a reaction according to (2) can take place, more inductor than acceptor will be found oxidised in the system.

In addition to the cases cited above, the following examples indicate the diversity of these coupled reactions:

Actor.	Inductor.	Acceptor.
$HgCl_2$	Na_2SO_3	Na_3AsO_3
O_2	$Ce(OH)_3$	$Ni(OH)_2$
O_2	Na_2SO_3	Na_3AsO_3
O_2	$SnCl_2$	$Fe(NH_4)_2SO_4$
O_2	Na_2SO_3	$NaNO_2$

The conditions under which a coupled reaction consisting of two reactions exemplified by Equations (1) and (3) may be converted into a catalytic reaction in which the inductor A becomes a catalyst, as is indicated by Equation (4), have been investigated by Goard and Rideal,[1] who showed that if the oxidation potentials of the system conformed to the following scheme:

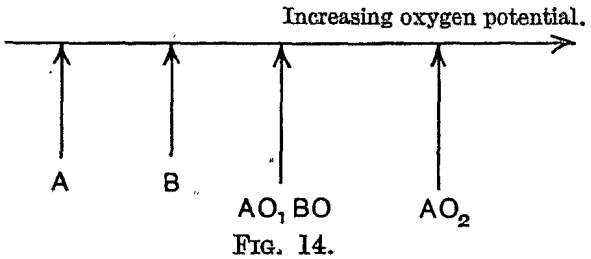


FIG. 14.

the reaction was coupled; whilst reduction of the oxidised inductor AO would be achieved and the reaction rendered catalytic, in that the inductor would function as a catalyst for the oxidation of the acceptor B if the oxidation potential of the reactants conformed to the scheme

[1] *Proc. Roy. Soc.* (*A*), 1924, **105**, 134, 148.

(Fig. 14A). It is clear that the acceptor B can now reduce the oxidised inductor AO back to the original state A, in which it is capable of forming anew the unstable peroxide AO_2.

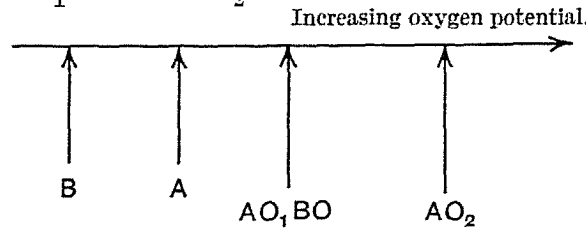


FIG. 14A.

This transition from a coupled to a catalytic oxidation process and vice versa, in agreement with the hypothesis of the order of the oxidation potentials outlined above, was examined for two particular cases.

Salts of the colourless cerous oxide Ce_2O_3 are found to undergo coupled oxidation with arsenites in alkaline solution, but catalytically accelerate the oxidation of a number of sugars such as glucose, lactose, and fructose.

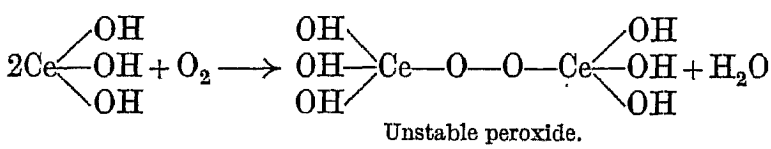
The oxidation potentials were found to be in the order

(i.) Cerous salt (inductor), arsenite (acceptor), equilibrium mixture, perceric salt.

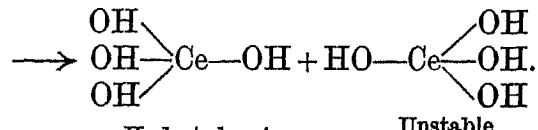
(ii.) Sugar (acceptor), cerous salt (inductor and catalyst), perceric salt.

In the case of Schönbein's reaction, the separation of iodine from potassium iodide in the presence of ferrous salts and hydrogen peroxide, it was found that in neutral solution the oxidation potential of the inductor, the ferrous salt, lay far below that of the acceptor, potassium iodide, and that the reaction was consequently coupled. In acid solution, on the other hand, the relatively high oxidation potential of the inductor leads to its constant regeneration in presence of excess of the acceptor, so that the reaction becomes catalytic.

The actual course of change in the case of cerous compounds acting as a part of a coupled reaction, *e.g.* in the oxidation of arsenites, has been examined in detail by Job,[1] who has identified the existence of cerium salts in three states of oxidation—the colourless cerous salt corresponding to Ce_2O_3, the yellow ceric salt CeO_2, and a red peroxide. He suggests the following mechanism of change :



Unstable peroxide.



Hydrated ceric. Unstable hydroperoxide.

[1] *Loc. cit.*

While the intermediate peroxide theory appears to be well substantiated, and the theoretical anticipations of the conditions of change from a coupled to a catalytic oxidation experimentally verified, there are nevertheless certain points which still await definite experimental verification.

We have noted that Moureu and his co-workers have come to the definite conclusion that the process of simple oxidation of a substance such as benzaldehyde proceeds through two steps, exemplified by the equations

$$(1) \quad A + O_2 = AO_2,$$
$$(2) \quad AO_2 + A = 2AO.$$

The question whether a reaction according to (2) actually takes place has not yet been definitely answered. As has already been indicated, Titoff's experiments on the oxidation of sulphites indicated the probability at least, if not the necessity, for a catalyst to be present. It would appear equally plausible to assume that the mechanism postulated by Moureu really involves two steps, in which a catalyst C plays a part:

$$AO_2 + C = AO + CO,$$
$$CO + A = C + AO.$$

If positive catalysts are actually always required to cause the interaction of the unstable peroxide with the unoxidised substance so as to form an "electrical circuit", the many difficulties associated with the remarkable effects of small traces of inhibitors already referred to (pp. 142-157) do not arise.

The second point on which conclusive evidence is still lacking is how far the original hypothesis of the formation of an unstable peroxide by direct interaction of the substance with molecular oxygen is tenable. Armstrong rejects the hypothesis, in that according to his view all these processes must be electrolytic in character. Thus the inhibition by hydrogen cyanide of the decomposition of hydrogen peroxide by colloidal platinum is expressed as the formation of unstable "perhydrols" with their reversible interaction:

$$\begin{matrix} & OH & HO \ldots H & HO & .OH \\ Pt & + & & + & = HPt.OH + 2H_2O, \\ & H & HO \ldots H & HO & .OH \end{matrix}$$

$$\begin{matrix} .OH & H \ldots OH & OH \\ HPt.OH + & & + OH(CNH)H \\ .OH & H \ldots OH & OH \end{matrix}$$

$$= Pt\begin{matrix} OH \\ H \end{matrix} + 2H_2O + 2H_2O_2 + HO(CNH)H,$$

and similar hydroxylations effected by the depolarising effect of oxyge on the elements of water acting as part of an electrical circuit must b imagined as the mechanism of formation of the peroxides required fo these processes. Some interesting peculiarities in oxidation catalysi are to be noted in the investigations of Rutter [1] on catalysis wit vanadium salts. Many examples of the effectiveness of these compound as oxidation catalysts are to be found, such as the oxidation of sulphu dioxide, naphthalene, and benzene with air, of aniline by chlorates, o mercury by bromates or hydrogen peroxide, and in the catalyti decomposition of hydrogen peroxide.

The general method of representation of these catalytic change may be written

$$MO_2 + V_{lower} \longrightarrow MO + V_{upper},$$
$$V_{upper} + X \longrightarrow XO + V_{lower}.$$

The necessity for the oxidation potential of V_{upper} to be less than tha of MO_2, but less than that of XO, has already been indicated if catalysi is to occur at all. It is also clear that in addition the question o reaction velocity in the chemical reactions involved must be considered

Thus we find V^{III} can, like I^{I} and Fe^{II} ions, reduce certain highe oxides. V^{III} ions, however, reduce $HClO_3$ more rapidly than I^{I} o Fe^{II} ions, but reduce $H_2S_2O_8$ less rapidly than these ions.

The interaction between $HClO_3$ and HI is relatively slow, and is thu effectively catalysed by vanadium salts on account of the speed o the reactions $V^{III} + HClO_3$, $V^{IV} + HClO_3$, and $V^{V} + HI$. On the othe hand, the reactions $FeSO_4 + H_2S_2O_8$ or $HI + H_2S_2O_8$ are scarcely affecte by vanadium salts owing to the slow speed of the primary reactio $V^{\cdots} + H_2S_2O_8$ compared with that of the ferrous or iodine ion. Rutte noted also that such catalytic oxidations might be attended with primary coupled reaction, as in the following case :

$$\underset{\text{Actor.}}{\text{Chromic acid}} + \underset{\text{Acceptor.}}{HI} + \underset{\text{Inductor.}}{V^{III} \text{ or } V^{IV}} \longrightarrow I_2 + V^{V} + \text{chromium salt.}$$

The reaction proceeds in the following steps :

$$CrO_3 + V^{III} \longrightarrow Cr_2O_5 + V^{V}. \qquad Cr_2O_5 + I^{I} \longrightarrow Cr_2O_3 + I.$$

Such reactions may be attended by periodic phenomena, as noted b Bray,[2] who found that under certain conditions the catalytic decom position of hydrogen peroxides by iodates, according to the reactions

$$5H_2O_2 + I_2 = 2HIO_3 + 4H_2O,$$
$$5H_2O_2 + 2HIO_3 = 5O_2 + I_2 + 6H_2O,$$

acquired a periodic character. There is, however, a possibility tha such periodicity may be due to inhomogeneity of the reacting solution

[1] Dissertation, Berlin, 1906. [2] *J. Amer. Chem. Soc.*, 1921, **43**, 1262.

The Drying of Oils

The use of siccatives to accelerate the drying of the oil in paints and varnishes is a very usual one, and has been the subject of much experimental investigation. It has long been known that linseed oil, when exposed in thin films to the air, undergoes slow oxidation, a property used both in the paint and varnish industry as well as in the manufacture of linoleum.

Lippert,[1] Weger,[2] and Kissling[3] showed that the "drying" was virtually a process of autoxidation, and that linseed oil could absorb or combine with more than 20 per cent of its weight of oxygen.

The reaction velocity of this process of autoxidation was first

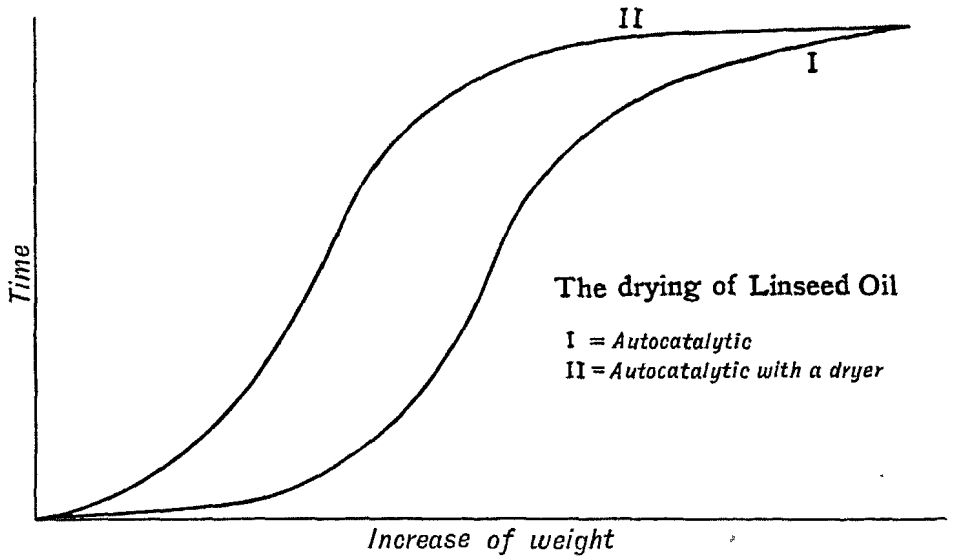


Fig. 15.

examined by A. Genthe,[4] who found that the increase of weight–time curve exhibited the usual sinuous character of an autocatalytic reaction (Fig. 15).

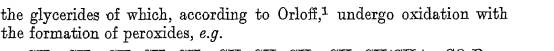
It had therefore to be assumed that in the oxidation of linseed oil to linoxyn, a product, either an intermediary or the result of some side reaction, was formed, which exerted a catalytic function on the autoxidation of the oil.

If a, b be the initial concentrations of linseed oil and autocatalyst respectively, then the rate of oxidation of the oil after a time t when x of the linseed oil has already been oxidised, is given by the equation

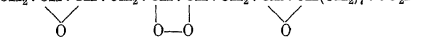
$$\frac{dx}{dt} = K(a-x)(b+x),$$

[1] *Zeitsch. angew. Chem.*, 1898, **11**, 412.
[2] *Chem. Rev. Fett-Harz-Ind.*, 1899, **4**, 30[illegible]1.
[3] *Zeitsch. angew. Chem.*, 1891, **4**, 395.
[4] *Ibid.*, 1906, **19**, 2087.

the glycerides of which, according to Orloff,[1] undergo oxidation with the formation of peroxides, *e.g.*

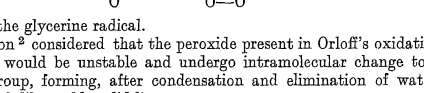


and

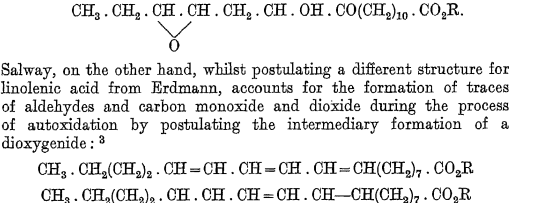


R being the glycerine radical.

Fahrion [2] considered that the peroxide present in Orloff's oxidation products would be unstable and undergo intramolecular change to a ketoxy-group, forming, after condensation and elimination of water, the varnish-like stable solid linoxyn :



Salway, on the other hand, whilst postulating a different structure for linolenic acid from Erdmann, accounts for the formation of traces of aldehydes and carbon monoxide and dioxide during the process of autoxidation by postulating the intermediary formation of a dioxygenide : [3]



Linoxyn would thus be, substantially, a condensed aldehyde in unchanged linseed oil.

On the addition of very small quantities of siccatives such as the salts of manganese, lead, and, more rarely, cobalt, vanadium, and

[1] *J. Russ. Phys. Chem. Soc.*, 1910, **42**, 658. [2] *Zeitsch. angew. Chem.*, 1910, **23**, 723.
[3] See Salway and Kipping, *J. Chem. Soc.*, 1909, **95**, 166.

uranium, the drying process is considerably shortened and S-shaped curve follows that indicated by II.[1]

It is still a matter of dispute whether the siccative is a cat *per se* for the oxidation of linseed oil, or whether it catalytically ha the formation or stabilises the presence of the autocatalytic perc and thus exerts a pseudo-catalytic function.

If initially present in very large quantities the quantity autocatalyst may be neglected and the form of the curve woul represented by the simple equation

$$\frac{dx}{dt} = k'(a - x).$$

Some experiments, however, by Rideal point to the persistenc the "period of induction", followed by a rapid rise in the valu dt/dx; we must therefore assume that the siccative is pseudo-catal in behaviour and serves either to stabilise or assist in the formatio the autocatalytic peroxide.

The metallic salts of weak acids are usually employed, *e.g.* borates. These, however, suffer from the disadvantage of b insoluble in the oil. Under these conditions, the influence of siccative present as a heterogeneous phase in the oil is not very mar and, at the same time, the small solid particles present in the oil, e when they are chemically inert, as, for example, in the case of si or barytes, act as negative catalysts,[2] since they assist in the composition of the autocatalytic peroxides. For this reason solu organic salts, usually the soaps, are generally employed. Lead ole cobalt linoleate, and manganese rosinate are examples of such soaps

Ingle,[3] and Mackey and Ingle,[4] as a result of a long series investigations on the action of siccatives, arrived at the follow conclusions:

(1) In its oil soluble form, *i.e.* as a soluble metallic soap, th metals which exist in more than one state of oxidation act as dri provided that the salts of the lower oxides are more stable than th of the higher oxides.

(2) Metals which form a number of oxides are more active than t mono- or divalent metals.

The results obtained in the investigations of Ingle are summaris in the following table (Fig. 16). The black lines indicate the ti required for 7 grms. of cotton-wool, oiled with 14 grms. of linseed (iodine value 178), and mixed with 2 per cent of metallic soap, to atta a temperature of 200° in a cloth oil-tester. The shaded lines give t corresponding times required for 14 grms. of olive oil (iodine value 5 to attain the same temperature under similar conditions.

Copper proved to be somewhat erratic in behaviour, acting first

[1] See p. 221, *ante*.
[2] Gardner, *J. Ind. Eng. Chem.*, 1914, **6**, 91.
[3] *J. Soc. Chem. Ind.*, 1916, **35**, 454.
[4] *Ibid.*, 1917, **36**, 317.

an accelerator and subsequently inhibiting the oxidation. It was shown that this action was due to the precipitation of cuprous oxide in the oil on elevation of the temperature.

It will be noted that both sodium and silver show catalytic activities which are considerably higher than would be expected from Mackey and Ingle's generalisations, and for which no explanation is as yet forthcoming.

Further investigation on the influence of H′ and OH′ on the reaction velocity may indicate that the optimum conditions are to be found when the oil, which always contains small quantities of water

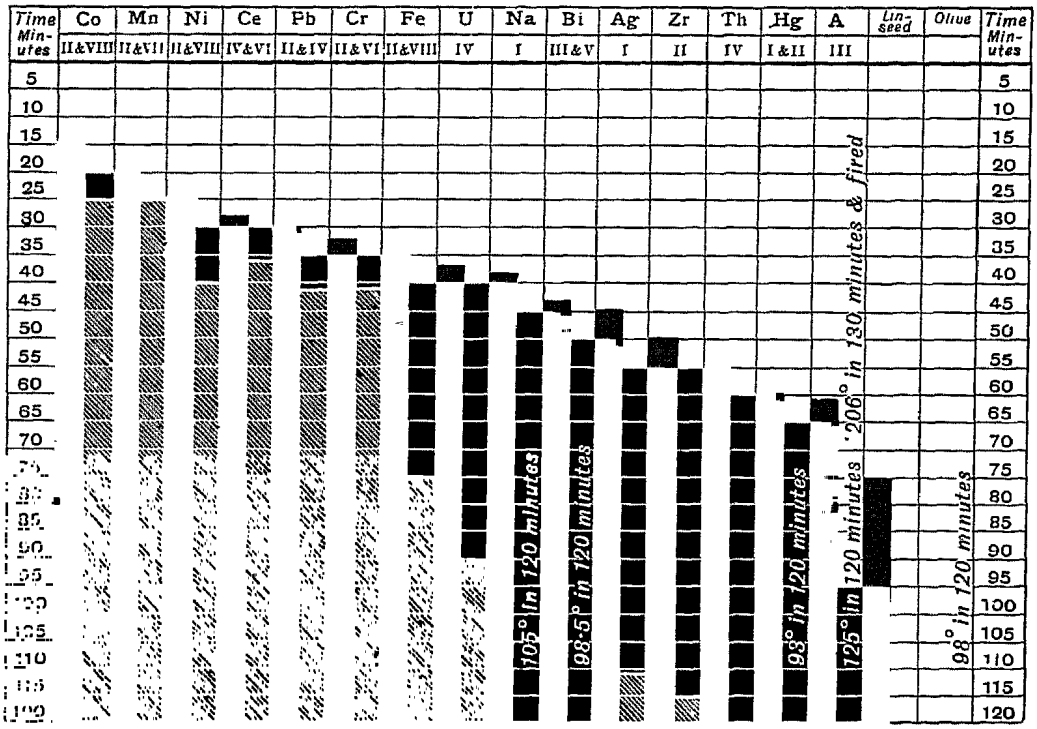


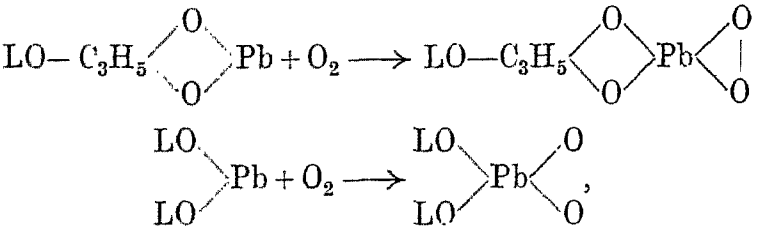
FIG. 16.

resulting from the autoxidation, is slightly alkaline, the sodium soap serving to neutralise the small quantities of relatively strong acids, such as acetic and formic acid, which are by-products of the oxidation. In the case of the silver soap, the precipitation of colloidal silver, especially since Cu_2O has been shown to be formed above 100°, may be expected, and this would probably show enhanced activity as an oxygen carrier.

Ingle attributes the action of siccatives to the intermediary formation of peroxides. Thus, on the addition of litharge to linseed oil partial saponification of the glyceryl linolenate results in the formation of lead linolenate and glyceryl plumbo-linolenate :

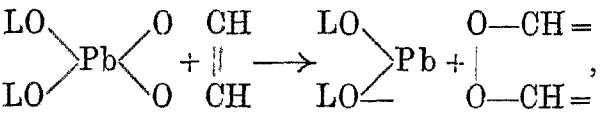
$$C_3H_5(OL)_3 + 2PbO \longrightarrow PbO_2 \,.\, C_3H_5OL + Pb(OL)_2.$$

Both these lead salts can form compounds with atmospheric oxygen to give compounds of tetravalent lead:



in which L denotes the linolenic acid radical.

Further reaction may then occur with the unsaturated double linkages of the fatty acids and glycerides present in the oil:



and thus hasten the normal oxidation velocity of the oil.

CHAPTER VIII

HYDROGEN AND HYDROGENATION

The Manufacture of Hydrogen

The increasing employment of hydrogen in modern technical processes, as, for example, in the hydrogenation of oils and the fixation of atmospheric nitrogen as ammonia, has created the problem of a cheap hydrogen supply. Moreover, the demand in catalytic hydrogenation processes for purity of materials necessitates in many cases the production of hydrogen in a high degree of purity.

The sources of hydrogen supply are various. Electrolytic hydrogen, naturally, can be readily obtained with the necessary degree of purity, but the cost factor in the majority of circumstances renders its use prohibitive. By another method, in use on a large technical scale, hydrogen is produced by the decomposition of steam in presence of heated iron, the resulting oxide of iron being reduced to the metallic condition by means of water gas. With careful regulation, this process may be made to yield hydrogen of the requisite purity. Without due attention, however, the presence of prohibitive concentrations of carbon monoxide in the gas, resulting from the action of steam on carbon deposited in the iron from the water gas during the reducing phase, may render the hydrogen unsuitable for use in certain catalytic operations. Furthermore, the economy of the process is, at present, low, and the cost factor, therefore, somewhat high.

The analogous process of Bergius, already investigated upon a small technical scale, generates hydrogen under high pressure and with great purity, by the action of liquid water upon finely divided iron at moderate temperatures in closed steel bombs. The pressures employed are generated by the reaction itself and are sufficient to maintain the water in the liquid state. The temperatures required, apart from the initial heat necessary to start the reaction, are maintained by the exothermicity of the reaction. Like the previous method of preparation, the process is discontinuous, the oxide of iron produced simultaneously with the hydrogen requiring subsequent reduction to the metallic state.

Hydrogen may also be produced from water gas by liquefaction of the carbon monoxide at the temperatures of liquid air boiling under reduced pressures. By this method complete separation of the constituents of the water gas is not readily attainable and, in common practice, a hydrogen containing from 2 to 3 per cent of carbon monoxide is generally obtained. A more complete separation of the two gases may only be obtained with a prohibitive decrease in the yield of hydrogen, since a mixture of hydrogen with 2 per cent of carbon monoxide behaves almost exactly like hydrogen in its physical properties. Actually, the yield of hydrogen would be considerably increased if a 95 per cent hydrogen were obtained by the liquefaction process, the remaining 5 per cent of carbon monoxide being subsequently removed by other means.

The water-gas catalytic process.—The most recent technical method for the production of hydrogen, and in many ways the most promising as regards cheapness of production, involves a catalytic operation using water gas and steam as the reaction materials. In the presence of suitable catalytic agents, at regulated temperatures, carbon monoxide and steam react to yield carbon dioxide and hydrogen. Utilising water gas, therefore, a gas rich in hydrogen would result, the problem of further purification involving the removal of the carbon dioxide formed and of the unconverted carbon monoxide.

The reaction occurring, which may be formulated by means of the equation

$$CO + H_2O \rightleftarrows CO_2 + H_2,$$

is in reality an equilibrium process, the direction of the reaction being governed by the temperatures maintained and the concentrations of the respective components. The equilibria obtaining at various temperatures may, in the absence of experimental data over the whole range of temperatures required, be calculated from the experimental work of Hahn[1] at higher temperatures. In this way the following approximate values for the equilibrium constant

$$K = \frac{p_{H_2O} \times p_{CO}}{p_{H_2} \times p_{CO_2}}$$

at the various temperatures are obtained:

T.	400°	500°	600°	700°	800°
K.	0·05	0·1	0·3	0·6	0·9

From these figures it is obvious that high temperatures favour the production of carbon monoxide in agreement with experience in water-gas manufacture. Lower temperatures favour the production of carbon dioxide and hydrogen. The lower the temperature at which the water-gas reaction occurs, the greater will be the conversion of carbon monoxide to dioxide with the corresponding increase in yield

[1] See Haber, *Thermodynamics of Technical Gas Reactions.*

and purity of hydrogen. On the other hand, decrease of temperature slows down the reaction velocity, so that, in practice, a low limit to the temperature will be set below which attainment of equilibrium conditions requires the presence of catalytic agents. It is obvious from these facts that, for the successful production of hydrogen from water gas, catalytic agents are required which will rapidly promote the reaction at as low a temperature as possible.

A considerable patent literature relative to this process already exists. The basic patent for the production of hydrogen from gases containing the same in admixture with carbon monoxide and hydrocarbons was granted to Mond and Langer.[1] According to this invention, the gases were to be passed with excess of steam over heated catalysts, for example, nickel at temperatures of 350°-400°, cobalt at 400°-450°. The hydrocarbons were said to be decomposed, while the carbon monoxide was converted to the dioxide, which was thereupon removed. It was subsequently claimed that the gas produced was almost free from carbon monoxide. Elworthy suggested the employment of nickel or iron in a similar manner with a mixture of water gas and steam. A patent of Pullman and Elworthy [2] proposes to separate the carbon dioxide and hydrogen by processes of diffusion and of fractional solution. In 1907 Vignon applied for a patent [3] for a process as above, using iron or oxides or platinum at red heat. The patent was not granted. Ellis and Eldred [4] employed nickel, iron, or manganese for catalytic agents of the water-gas-steam reaction, using a specially designed superheated reaction chamber. Näher and Müller [5] suggest the use of a contact mass of rhodium or palladium asbestos at a working temperature of 800°. They claim a product with less than 0·4 per cent of carbon monoxide. It is obvious that at a temperature of 800° such a low content of carbon monoxide can only be obtained by the use of large excesses of steam, which would render the process economically impossible. More recently a considerable number of patents have been obtained by the Badische Anilin- und Soda-Fabrik relative to the process, which has been established by them on a commercial basis. B.P. 26770/1912 calls for the carrying out of the process under pressures of 4-40 atmospheres at temperatures between the limits of 300° and 600°, using nickel and cobalt as catalysts. The increase in pressure improves both the reaction velocity and the heat regeneration. So conducted it was claimed to be specially useful for gases with small carbon monoxide content. Later, in 1912,[6] an improvement was patented for the maintenance of the requisite temperature in the catalytic mass by the addition of air or oxygen, which, combining with some of the hydrogen, generated sufficient heat to enable the process to be maintained continuously, especially if only small amounts of carbon monoxide were present. A patent of 1913 [7]

[1] B.P. 12608/1888. [2] B.P. 22340/1891. [3] B.P. 20685/1907.
[4] U.S.P. 854157/1907. [5] B.P. 20486/1911. [6] B.P. 27117. [7] B.P. 27955.

by the same company deals with suitable catalysts, the basis of which was oxide of iron with suitable binding agents. B.P. 8864/1913 is concerned with catalysts containing nickel, cobalt, and similar substances, which apparently tend towards the simultaneous production of methane, since B.P. 27963/1913 deals with catalysts which do not produce methane by side reaction. The materials here cited as catalysts are numerous and involve as basic substance principally iron oxide in admixture with one or more substances acting as promoters of the activity of the iron oxide. Chromium, nickel, aluminium, thorium, zinc, lead, uranium, and other oxides are cited in this connection. A later patent[1] returns to the claims of B.P. 27955/1913, amplifying them by claiming, for use as catalysts, oxide, hydroxide, and carbonaceous iron ores employed either in bulk or brought into suitable form by powdering and admixture with binding agents. The minerals employed should preferably be free from sulphur, chlorine, phosphorus, and silicon, though small amounts of these are said to be permissible. It is insisted, with regard to the production of all these catalysts, that high temperatures should be avoided in the course of preparation, and a limit is set at preferably below 650°. It is obvious that such limitations exclude from use the oxide of iron obtained by the roasting of pyrites ores. The utilisation of this material for catalytic preparations is the subject of a patent by Buchanan and Maxted,[2] who claim the use of the oxide of iron obtained from sodium ferrite as catalyst. The material is prepared by fusion of burnt pyrites with sodium carbonate at elevated temperatures, followed by lixiviation of the mass thus obtained. The mass of iron oxide so prepared, and containing some undecomposed ferrite, is claimed to give good conversion at moderate temperatures. A succeeding patent of Buchanan and Maxted[3] claims the use of metallic couples as improved catalysts. Thus, by reduction of the iron oxide obtained in the manner cited in the previous patent and by immersion of the iron thus produced in a solution of copper salts, a metallic iron-copper couple is obtained with which improved conversion at increased velocities is claimed.

The actual material used, in technical operation, will depend not only on catalytic activity but also on factors such as robustness of catalytic material and durability towards impurities in the raw materials used for manufacture. Oxides of iron, either from minerals, such as spathic ore, or prepared from iron compounds, are the main constituents of technical catalysts. Promoters, such as chromium and cerium oxides, improve the oxides of iron markedly. The technical details of the process need not be given here, since they have been fully treated in a number of publications.[4]

Assuming a working temperature of 500° and a catalytic agent

[1] B.P. 16494/1914. [2] B.P. 6476/1914. [3] B.P. 6477/1914.

[4] See, for example, Taylor, *Industrial Hydrogen*, chap. iii. (Chemical Catalog Co., New York, 1922).

capable of producing equilibrium at rapid gas velocities, it is interesting to note the products to be obtained from a commercial blue water gas containing, say, 40 per cent of carbon monoxide. At 500°

$$k = \frac{p_{H_2O} \times p_{CO}}{p_{H_2} \times p_{CO_2}}$$

is approximately equal to 0·1, so that with equal concentrations of steam and hydrogen in the exit gases it is obvious that $p_{CO}/p_{CO_2} = 0{\cdot}1$; that is, there would be approximately 4 per cent of carbon monoxide in the residual products when the steam was eliminated. In practice it is customary to reduce this percentage by employing excess of steam, the amount of reduction being governed by the amount of steam used. Apparently the best economic balance is secured by employing sufficient steam to reduce the carbon monoxide content of the residual gas to 2 per cent. This involves, according to the equilibrium data, a steam : hydrogen ratio in the exit gases of 2 : 1 or an initial ratio of water gas to steam of 1 vol. water gas to $2\frac{1}{2}$ vols. of steam, according to the equation

$$\underbrace{H_2 + CO}_{\text{Water gas.}} + 5H_2O \rightleftharpoons 2H_2 + CO_2 + 4H_2O.$$

Using these approximate quantities, a typical analysis of the resulting gas will be somewhat of the order $H_2 = 65$ per cent, $CO_2 = 30$ per cent, $CO = 2$ per cent, N_2, etc., 3 per cent.

The thermal balance of the process may now be considered. The reaction occurring,

$$CO + H_2O \longrightarrow CO_2 + H_2,$$

is exothermic, 10,000 cals. being liberated per molecule of carbon monoxide converted. With good heat exchangers capable of yielding a 75 per cent heat regeneration, the evolution of heat is sufficient to cover all conduction and radiation losses. Only at starting is preheating requisite, for which purpose water gas may be burnt. Subsequently the mixed water gas and steam pass through heat exchangers, in which they are brought to the reaction temperature of about 500° by means of the heat of the exit gases passing in the reverse direction and leaving the heat exchangers at a temperature of approximately 100°. With such a procedure the process is continuous, a factor of considerable advantage as compared with other processes of hydrogen production.

The economy of the process may be illustrated from another point of view. Consideration of the reaction equation will show that, theoretically, for the production of 1 volume of hydrogen, 1 volume of water gas is required. In practice it is claimed that 1·1 volumes of water gas are sufficient. This is in marked contrast to the conditions obtaining in the steam-iron process, in which from 2 to 4 volumes of water gas are required, according to practical experience, for the production of 1 volume of hydrogen. As regards the economy of steam

in the process, it must also be observed that although an excess of steam is required in this process to decrease the final carbon monoxide content, the steam consumption is much less than in the intermittent steam-iron process, in which, as at present employed, as much as three or four times the theoretical amount of steam required is employed for the production of unit volume of hydrogen.

A further advantage of the process exists in that crude water gas may be employed, no special purification other than the removal of mechanical impurities, such as flue dust, being required. This economy is realisable owing to the fact that all the organic sulphur compounds present in the gas are converted catalytically into sulphuretted hydrogen. This process of sulphur conversion is interesting in other connections and is dealt with in more detail elsewhere in this book. The sulphuretted hydrogen formed in this manner, together with that originally present in the gas, can readily be removed from the resulting gas mixture along with the carbon dioxide. Obviously, therefore, the hydrogen obtained, being sulphur-free, is especially suitable for certain catalytic operations, as, for example, ammonia synthesis.

The disadvantages associated with the catalytic process may be enumerated. In the first place, there is the removal of the carbon dioxide, which forms upwards of 30 per cent of the exit gases from the condensers. Actually this is carried out in practice by a system of counter-current water-washing under pressures of about 30 atmospheres. The system is well tried and yields hydrogen with a carbon dioxide content of less than 1 per cent, which residue may be subsequently removed by lime or alkalis. If the hydrogen has afterwards to be used in the compressed state, the compression costs are negligible. Large quantities of water must necessarily be conveniently to hand, however, for the operation of the process. Part of the energy necessary for pumping the water is recoverable by making the issuing water work an appropriate motor. By means of a Pelton wheel arrangement 30 to 50 per cent of the energy may be recovered. Simultaneously with the carbon dioxide, sulphuretted hydrogen is also removed. A certain loss of hydrogen occurs during the process of water-washing, presumably of the order of 10 per cent.

The removal of the unconverted carbon monoxide forms a second obstacle to the utilisation of the catalytic process. Numerous methods have been suggested for effecting this. Certain processes involve methods of absorption, for example, by ammoniacal cuprous salts under pressure. The conversion of carbon monoxide to sodium formate by hot caustic-soda solutions under pressure has also been utilised for removal. The gases when freed from carbon dioxide and sulphur compounds are also sufficiently pure to enable one to remove the carbon monoxide by conversion at the expense of hydrogen to methane, using a nickel catalyst. The Badische patent [1] previously cited reduces

[1] B.P. 26770/1912.

the monoxide content of the gas by repetition of the main catalytic process under pressures of 4-40 atmospheres. Preferential combustion of the carbon monoxide in the hydrogen has been proposed by Harger and Terry[1] and applied to the particular product from the water-gas catalytic process by Rideal and Taylor[2] with a high-temperature (200° C.) catalyst of iron-chromium-cerium oxides, and by Lamb, Scalione, and Edgar[3] with a catalyst consisting of copper and manganese oxides at temperatures below 100° C. It is obvious that the particular process adopted may be governed by various factors operating to determine the choice.[4]

For certain purposes a further disadvantage of the catalytic process lies in the presence in the final hydrogen of the inert gases, *e.g.* nitrogen, methane, etc., present in the original water gas. For ammonia synthesis the presence of nitrogen is no disadvantage. In other catalytic operations it may act as a diluent, and in circulating systems tends—as does methane also—to accumulate in the gaseous system and so finally bring about a stoppage in the process for the rejection of the diluted hydrogen, or a constant loss of spent gas by continuous removal from the circulatory system.

In spite of these disadvantages it would seem that the continuous catalytic process is the cheapest and most promising of the processes for large-scale hydrogen production. It is a process also which still offers considerable possibilities for development and improvement, mainly in the treatment of the gases obtained from the contact mass. The efficiency of the process up to this stage may be regarded as already very high.

The problem of removal of the large quantities of carbon dioxide obtained by catalytic conversion of water gas and steam is the object of another series of patented processes employed upon a technical scale by the Griesheim Elektron Co.[5] The catalytic material is lime suitably activated by admixture of substances like oxide of iron. Operating at temperatures of 400°-500°, conversion to carbon dioxide and hydrogen of the water gas and steam is readily attained. The lime at these temperatures absorbs the carbon dioxide, yielding carbonate, since only above 600° does the dissociation pressure of calcium carbonate become marked.[6] Absorption of the carbon dioxide disturbs the equilibrium which otherwise would prevail, and so the carbon monoxide is thereby more completely removed. Also, the resulting gas does not contain the large quantities of carbon dioxide obtained in the process previously considered. On the other hand, it is obvious that owing to the conversion of the lime into carbonate the process is necessarily

[1] B.P. 12709/1917. [2] *Analyst*, 1919, **44**, 89.

[3] *J. Amer. Chem. Soc.*, 1922, **44**, 738.

[4] For a complete treatment of the industrial problems in the manufacture of hydrogen by the various processes, see Taylor, *Industrial Hydrogen*, A.C.S. Monograph (Chemical Catalog Co., New York, 1921).

[5] B.P. 2523/1909. [6] Johnston, *J. Amer. Chem. Soc.*, 1912, **32**, 946.

discontinuous, the lime requiring regeneration by heating to more elevated temperatures. The employment or rejection, therefore, of such a process as an alternative to the catalytic process previously considered hinges on the economy of the regeneration of the lime catalyst as against the process of water-washing under pressure. It will be obvious that for a large-scale hydrogen plant the lime required will be enormous, of the order of 100 lbs. of lime for 1000 cubic feet of water gas containing 45 per cent of carbon monoxide, assuming that as much as half the lime may be converted to carbonate without impairing its ability to remove the carbon dioxide from the gases produced. It is doubtful whether the expense of regeneration of such quantities of lime would compete in a large technical unit with the continuous system of removal of carbon dioxide by counter-current water-washing. Disintegration of the lime during the process also forms a further disadvantage in practical operation.

The original patents for the lime process were due to Tessié du Motay (1880). The improvement of the Griesheim Elektron Co., which consisted in the addition of 5 per cent of iron powder to act as an accelerator, was studied theoretically by Engels,[1] who found that equilibrium conditions could be obtained at markedly increased velocities of passage of the steam-water-gas mixture when such activators were present. It is obvious that the addition of the iron tends to promote the water-gas reaction as in the continuous catalytic process detailed above, and, therefore, also promotes the attainment of equilibrium with the lime. Doubtless, too, it would be found that the active catalysts (iron oxide with promoters) of the continuous process would also accelerate considerably the lime process. Further, a method of procedure should be possible in which the steam-water-gas mixture passed first at 400°-500° over an efficient catalyst for the water-gas reaction, then over lime in a second chamber maintained at the same temperature to remove the carbon dioxide, and finally over a further mass of the original catalytic material in which the residual carbon monoxide should be further converted by steam to carbon dioxide, leaving only minimal quantities of carbon monoxide in the hydrogen obtained.

According to Mertz and Weith [2] carbon monoxide and steam react when passed over soda-lime at temperatures of 300° and upwards. This method of manufacture of hydrogen has been suggested for technical operation by the Société générale des Nitrures of Paris [3] and the Chemische Fabrik Griesheim Elektron.[4] R. E. Wilson, Hasslacher, and Masterson [5] have studied the reaction in somewhat greater detail and conclude that soda-limes with high caustic-soda content are better than those with low, or than lime alone. The former give substantially complete removal of 2 per cent carbon monoxide in hydrogen mixtures

[1] Dissertation, Karlsruhe, 1911; *Chem. Abs.*, 1920, **14**, 599.
[2] *Ber.*, 1880, **13**, 719.
[3] D.R.P. 248290.
[4] B.P. 13049/1912.
[5] *J. Ind. Eng. Chem.*, 1923, **15**, 698.

at around 400° C. Small amounts of water vapour are helpful, though not essential, to the efficiency. These authors claim that the fundamental reaction for the removal of the gas at the higher temperatures is

$$CO + 2NaOH = Na_2CO_3 + H_2.$$

An alternative series of processes for the production of hydrogen-carbon dioxide mixtures from steam and coke are embodied in the patent claims of Dieffenbach and Moldenhauer. Instead of employing catalytic agents to bring about the water-gas reaction, these claimants propose to facilitate, by addition of catalysts, the reaction between coke and steam, so that it may be carried out at such low temperatures that the products of interaction are principally carbon dioxide and hydrogen. In B.P. 7719/1910 the addition of an alkaline hydroxide or salt, and especially a silicate, is suggested to enable the reaction between coke and steam to be effected within the temperature interval 550°-750°. In B.P. 7720/1910 the use of alkalis and alkali salts is suggested. The use of both alkali and lime, it is stated,[1] still further decreases the temperature at which steam and coke will react with rapidity. Neville and Taylor [2] have made a theoretical study of these patents and find that the alkali carbonates alone operate as really efficient catalysts. They showed that the catalysis involved an acceleration of the reaction between carbon dioxide and carbon rather than the effect of the catalyst on the water-gas reaction,

$$CO + H_2O = CO_2 + H_2.$$

It was shown that the absorptive capacity for carbon dioxide of a charcoal containing such catalysts was markedly greater than that of the same charcoal in the absence of such agents.

The steam-iron process of hydrogen manufacture.—As outlined in the introductory paragraphs of this chapter, the production of hydrogen by the action of steam on heated iron is already largely carried out in the industry. The main reaction which occurs may be represented by the equation

$$3Fe + 4H_2O = Fe_3O_4 + 4H_2.$$

By reduction, usually with water gas, of the oxide of iron thus obtained the iron may be regenerated and the cycle of operations repeated.

The original patents for the process are very old ; thus, for example, in B.P. 593/1861 Joseph Jacob claims the commercial production of hydrogen by the action of steam on iron filings or borings, or on iron crushed, ground, or pulverised. The heat of the retorts was to be maintained by combustion of a portion of the hydrogen produced ; the iron after oxidation was to be discharged from the retort.

The alternate reduction and steaming process was patented by Lewes.[3] Hills and Lane [4] and Hills and Monteux [5] utilise this principle

[1] B.P. 8734/1910.
[2] *J. Amer. Chem. Soc.*, 1921, **43**, 2055.
[3] B.P. 20752/1890 and B.P. 4134/1891.
[4] B.P. 10356/1903.
[5] F.P. 386991/1908.

in specially designed apparatus for commercial production. The earlier types of plant have been considerably modified in detail as a result of accumulated experience, but the principle of operation remains substantially the same. Further economies of operation are claimed in the numerous patented details of Messerschmidt.[1]

According to the patent specification of Lewes, iron borings may be employed for the reaction. Since the two phases of the process are, however, mainly surface actions, or at most penetrate but little into the interior of the material, recent practice has resolved itself into the substitution, for metallic iron, of iron in a porous or spongy condition which will offer a maximum of surface for a minimum of volume. The iron is therefore generally obtained by reduction of a mineral oxide or from carbonate ores such as spathic iron ore by reduction of the mass obtained after ignition and loss of carbon dioxide. In this way material possessing both porosity and resistance to disintegration is readily obtained. Roasted pyrites from which all sulphur and the volatile metals have been removed has also been proposed as the reaction material.[2] All such materials show a greater or less tendency to lose their activity with repeated oxidation and reduction, and research into the causes thereof conducted on the large technical scale has shown it to be in part due to fritting of the surface. Part of the loss in activity is due to deposition of foreign bodies such as carbon, sulphur, etc., in the mass, but these may be removed by periodical heating in a current of air. The fritting, however, is permanent, and consequently many suggestions have been put forward to counteract this difficulty. They consist chiefly in the admixture with the iron of bodies which may either render the iron less fusible and less liable to soften with the temperatures employed, or which may catalytically assist the interaction of steam with iron so that good yields of gas may be obtained at lower temperatures than would normally prevail. Thus, Messerschmidt proposes [3] the use of natural ores of manganese and of manganese and iron to attain lower reaction temperatures. Dieffenbach and Moldenhauer [4] claim the use of alloys of iron with manganese, chromium, tungsten, titanium, aluminium, or other similar elements, as well as mixtures of the oxides briquetted or in other suitable form. The Badische Anilin- und Soda-Fabrik [5] propose iron oxide fused with refractory oxides such as zirconia and magnesia or with silicates. Jaubert [6] suggests the use of briquettes of iron oxide admixed with fire-clay, pumice, magnesia, and small amounts of the oxides of manganese, chromium, copper, and lead.

The gas obtained by the steam-iron process contains, after removal of small quantities of carbon dioxide and hydrogen sulphide by means of lime purifiers, upwards of 98 per cent of hydrogen. With careful

[1] See *J. Soc. Chem. Ind.*, 1914, **33**, 313; also Taylor, *Industrial Hydrogen, loc. cit.*
[2] B.P. 7849/1909. [3] F.P. 461480/1913. [4] D.R.P. 233347/1910.
[5] F.P. 440780/1912. [6] F.P. 418312/1909.

control a content of hydrogen as high as 99·75 can be continuously maintained without considerable increase in cost of production. Higher purity still, averaging 99·85-99·95 per cent of hydrogen, can be maintained by extraordinary precautions as to scavenging and by use of an elevated temperature coupled with frequent aeration of the contact mass. Naturally this increases considerably the cost of the gas owing to loss of yield, decreased activity of the iron due to fritting, and wear and tear of retorts at the high temperatures.

The main impurity of the gas is carbon monoxide resulting from interaction of the steam and carbon deposited in the iron during the reducing phase. This carbon results from the catalytic decomposition of the carbon monoxide [1] in the presence of iron, according to the equation

$$2CO \rightleftarrows C + CO_2.$$

In the steaming phase this carbon reacts with the steam to form carbon monoxide and dioxide, the concentration of steam present determining to a considerable degree the relative quantities of each in the issuing gas. As stated, the carbon dioxide is removed by means of lime purifiers or caustic-soda liquor, the carbon monoxide passing on with the hydrogen. Since the carbon in the iron mass is only incompletely decomposed by the steam, it gradually accumulates in the material and must therefore be occasionally removed by means of a hot air current.

The Bergius hydrogen process.—The patents of Bergius [2] relative to the manufacture of hydrogen by the action of liquid water, at elevated temperatures and therefore at high pressures, upon carbon or iron disclose certain interesting details as to the use of catalytic accelerators.

Bergius found that, at a temperature of 300° and at a pressure sufficient to keep the water liquid, carbon reacted almost exclusively with water to form a mixture of carbon dioxide and hydrogen, according to the equation

$$C + 2H_2O \longrightarrow CO_2 + 2H_2.$$

The addition to the water of small quantities of thallium salts was found to promote the reaction catalytically.

Employing iron, the corresponding reaction with liquid water also took place at the low temperature of 300°. Only in the initial stages of the reaction was heat required, the exothermicity of the reaction being sufficient to maintain the gas evolution. Pressures of 100 atmospheres or more were generated in the system and were reduced to the desired extent by occasionally blowing off the gas through a valve into cylinders in which the hydrogen could be stored already compressed. Catalytic acceleration of the reaction was secured by

[1] For equilibria, see Boudouard, *Compt. rend.*, 1900, **130**, 132; Rhead and Wheeler, *J. Chem. Soc.*, 1912, **101**, 831.

[2] D.R.P. 259030/1911, 254593/1911, and 262831/1912.

dissolving in the water neutral salts, as, for example, sodium chloride or acids, or by use of metallic couples such as iron-copper, or by the presence of a second metal such as nickel or platinum.

The Bergius iron-water process should be cheap and useful for small-scale hydrogen production under pressure where an expensive equipment is not possible. Regeneration of the finely divided iron metal employed can be effected by means of water gas, producer gas, or carbon at high temperatures.

Hydrogen production by catalytic decomposition of hydrocarbons.—In general, the saturated hydrocarbons, when subjected to a sufficiently high temperature, decompose into their elements, the carbon being deposited in an extremely fine state of division, hydrogen being simultaneously produced.[1] The temperature required for decomposition varies with the stability of the compound. Thus, methane dissociates rapidly only at 1200° to 1300°, its presence in a water-gas mixture being evidence that at the slightly lower temperature of water-gas manufacture the velocity of decomposition is comparatively low. On the other hand, acetylene decomposes at much lower temperatures, Pictet[2] effecting decomposition by passage through tubes heated initially to 500°. Since heat is evolved upon the decomposition of acetylene, the reaction continues automatically when once started. This process is generally applicable to endothermic hydrocarbons.

Numerous patented processes exist for the production of hydrogen by this method, the variations being, in the main, modifications for the better operation in technical practice. Thus the Carbonium Co., of Friedrichshaven, have decomposed acetylene under pressure by explosion with an electric spark. The hydrogen obtained is of high purity and has been employed for the filling of Zeppelins. The cost is, however, somewhat considerable, unless the lamp-black can be marketed. The pressures employed may be as much as 6 atmospheres.[3]

The decomposition of the light petroleum hydrocarbons is the subject of patents by Lessing[4] and by Pictet,[5] in which temperatures from 1000°-1350° are suggested. It is obvious that technical operation at such high heats is a matter of considerable difficulty, and it is not surprising that extended application has not yet been recorded. Recent work on the cracking of heavier hydrocarbon vapours will doubtless contribute greatly to the development of technique in this direction.

To bring about the decomposition of hydrocarbons at lower temperatures interaction with steam has been employed both with and without catalytic contact material. Pictet[6] produces thus carbon monoxide and hydrogen from hydrocarbon vapours and steam at high temperatures. The Badische Anilin- und Soda-Fabrik[7] suggest a

[1] Mayer and Altmayer, *Ber.*, 1907, 40, 2134.
[2] F.P. 421839/1910.
[3] Machtolf, D.R.P. 194301/1909.
[4] B.P. 15071/1909.
[5] B.P. 13397/1911.
[6] B.P. 14703/1911.
[7] B.P. 12978/1913.

refractory oxide such as magnesia impregnated with nickel oxide as catalyst for this process, at a temperature of 800°. Dieffenbach and Moldenhauer [1] use as catalyst wire gauze of nickel, cobalt, platinum, etc., for the same reaction, ensuring by the employment of the catalyst in such form a very short time of contact and thereby a sudden cooling of the reaction products. In this way, it is claimed, the carbon dioxide formed has little opportunity to be reduced to carbon monoxide. An important study of the many reactions involving the methane equilibrium, for example,

$$CH_4 + 2H_2O = CO_2 + 4H_2,$$
$$CH_4 + H_2O = CO + 3H_2,$$

has recently been completed.[2] This should prove useful in the theoretical study of this important technical problem.

Coke rendered white hot by an air blast has been proposed by the Berlin Anhaltische Maschinenbau A.G.[3] and by Ellis [4] as contact material for the production of hydrogen from paraffin hydrocarbons.

It should be possible with the aid of catalytic contact material to bring about the interaction of hydrocarbons with carbon dioxide to yield carbon monoxide and hydrogen, whence pure hydrogen could be obtained by processes described above. With unsaturated hydrocarbons this is apparently not difficult. A solution of the problem with the lower paraffins should yield to a systematic search for suitable catalytic material.

Hydrogenation

The systematic investigation of the problem of hydrogenation was undertaken at the close of the nineteenth century by Sabatier and his co-workers, of whom Senderens may principally be mentioned. Isolated observations had earlier been made and recorded concerning interaction of substances with hydrogen in the presence of a catalytic material. Generally, finely divided platinum was the agent employed. Its activity in promoting oxidation, as manifested in the early work of Davy and Döbereiner, had led to its trial in many other directions, sometimes with success. Thus, the catalytic reduction to ammonia of oxides of nitrogen by means of hydrogen in the presence of platinum sponge was recorded by Kuhlmann in 1838.[5] Carenwinder [6] showed its catalytic effect in promoting the combination of hydrogen and iodine. Applied to organic reactions, it was observed by Debus [7] that platinum black assisted the reduction of hydrocyanic acid to methylamine, and that ethyl nitrite could be transformed by means of hydrogen into ethyl alcohol and ammonia. The catalytic addition of hydrogen to

[1] D.R.P. 229406/1909.
[2] Neumann and Jacob, *Zeitsch. Elektrochem.*, 1924, **30**, 557.
[3] B.P. 2054/1914.
[4] U.S.P. 1092903/1914.
[5] *Compt. rend.*, 1838, **17**, 1107.
[6] *Ann. Chim. Phys.*, 1852 (iii.), **34**, 77.
[7] *Annalen*, 1863, **128**, 200.

unsaturated hydrocarbons and their transformation to saturated hydrocarbons was demonstrated by De Wilde in 1874,[1] platinum black being employed as agent.

By the researches of Sabatier and his assistants the catalytic method of hydrogenation has been generalised. From 1897 onwards, in a succession of researches published in the *Comptes rendus* of the Paris Academy of Sciences, by systematic application of the principle to the most diverse organic materials and employing various metals as catalytic agents, the wide applicability of hydrogenation has been made clear. The reactions have been studied generally in the vapour phase, volatile organic liquids being for the most part the materials employed in the investigation. Finely divided metals have formed the catalytic agents, and, of these, nickel, obtained freshly from the oxide by reduction, has proved to be the most efficient. The other elements which have found application are cobalt, iron, copper, platinum, and the platinum metals generally.

The simplicity of the studies carried out by Sabatier and his collaborators is striking. The procedure consisted essentially in passing hydrogen, admixed with vapours of the material to be investigated, through a tube containing the finely divided catalytic agent maintained at a controllable temperature, the products of reaction being suitably collected on emergence from the heated tube.

It was found to be essential that the hydrogen employed should be completely free from all impurities. Traces of sulphuretted hydrogen, of phosphine, arsine, and hydrogen chloride were found to act as catalyst poisons. Hydrogen, obtained by electrolysis and subsequently freed from traces of oxygen and moisture, was therefore largely employed, since by this process the other impurities could readily be avoided.

The preparation of hydrogenation catalysts.—Apart from the purity of the materials employed in hydrogenation processes, the most important factor in the conduct of such reactions is the preparation of the catalytic agent in a form suitable for use and of sufficient activity for the purposes required. Certain details relative to the preparation and properties of such agents are therefore apposite.

Nickel.—Catalytic nickel is the most important member of the group of hydrogenation catalysts. It is normally prepared by reduction of nickel oxide by hydrogen, an operation which can frequently be carried out in the reaction system. The oxide employed should be free, as far as possible, from the halogens and sulphur-containing compounds, since all these are catalyst poisons. Hence, where expense is not involved, the nitrate or an organic salt of nickel forms a suitable starting-point for the preparation of the oxide. The sulphate and chloride are the cheapest salts of nickel. When these are used the oxide is prepared by ignition of the hydrous oxide obtained by pre-

[1] *Ber.*, 1874, 7, 352.

pitation from solutions of the salts, followed by a thorough washing. some cases the carbonate is precipitated. The washing of such ecipitates should be continued until tests indicate freedom from the ion of the nickel salt and the cation of the precipitating agent. In e preparation of nickel supported on a finely divided support material e precipitation may be carried out in presence of the support, *e.g.* eselguhr, and the support-precipitate mixture washed together. In is way good distribution of the support may be obtained.

For nickel catalyst on coarser support material, such as pumice, atomite brick, and the like, the most convenient procedure is to npregnate the support with a hot, strong solution of the nitrate. A eliminary experiment will indicate how much liquid a given sample support material can take up to saturation, and this ratio of support liquid should be used. A concentration of 10 per cent nickel in the al product makes a good supported catalyst, and this figure deter-ines, therefore, the concentration of nitrate liquor employed. To sure thorough impregnation of the support, it is a useful practice heat the support above 100° C. and immerse it while still hot in the ckel nitrate solution.

The calcination of the nitrate, organic salt, or impregnated support yield oxide may be conducted in a casserole over a flame which will t permit too intense calcination. The actual temperature of con-rsion to oxide is not a matter of great moment, the subsequent duction temperature being the decisive factor. Some data on the fect of calcination temperature on the product have been recorded Brown and Henke.[1] They suggest limiting the temperature of nition to 450°, as sintering is appreciable above this temperature.

The presence of small amounts of promoters in nickel catalysts variably facilitates the preparation of an active material, and use of ese materials can be generally recommended both for supported and supported catalysts. Ceria, thoria, and alumina are strikingly good. edsforth [2] has recorded tests of many materials as promoters. They lp to produce a more porous oxide and a more active metal. Actual ncentrations of promoter cannot be laid down generally, but quantities rying between 0·5 and 15 per cent of the nickel metal are efficient. ey may be introduced as nitrates into the nickel solution.

The temperature of reduction of the oxide is the decisive factor in e preparation of a nickel catalyst. Quite generally it may be stated at the higher the reduction temperature, the less active will the sulting catalyst be. Supported catalysts are less sensitive to tem-rature than the unsupported material. For the latter a reduction mperature of 350° C. should never be exceeded, and the lower the mperature of reduction the more active the product, although the nger is the time consumed in the reduction process. A temperature

[1] *J. Physical Chem.*, 1922, **26**, 161, 272, 324, 631, 715; 1923, **27**, 52.
[2] *J. Chem. Soc.*, 1923, **123**, 1452.

of 300° C. probably represents a happy mean between the conflicting factors for the production of a catalyst of high activity. Supported materials do not reduce so readily as unsupported catalysts, and a temperature of 350° C. can be used with equanimity. Where extreme activity is not required, reduction of supported materials may be carried out as high as 450°-500° C. Promoted catalysts, both supported and unsupported, are very much less sensitive to overheating in the reduction process than are catalysts composed of nickel alone. When reducing at the higher temperature limits, it is good general policy in catalyst preparation to use a relatively slow stream of reducing gas.

Nickel catalysts may be prepared by direct reduction of the cyanide [1] and the chloride [2] with hydrogen. This latter method is remarkable in view of Sabatier's observation that the halogens act as poisons. It merits further test of this factor. Kelber showed that the same factors as regards reduction temperature and activity operated in the reduction of the cyanide as have already been laid down for oxide reduction.

It should be borne in mind that a catalyst cannot in general be raised above the temperature of reduction without loss of activity. This is especially true of unsupported catalysts. It must be remembered, in the conduct of markedly exothermic reactions, that the heat of reaction raises the temperature of the catalyst in spots considerably above the temperature recorded on the measuring instrument used, and such localised hot-spots diminish catalytic activity. The prolonged effect of even moderate temperatures is also to transform the catalyst to a more compact mass with a resulting decrease in efficiency.

Copper.—A copper catalyst is readily prepared in an active condition by reduction of the oxide at low temperatures. What has been said in the preceding paragraphs relative to precautions as to poisons, methods of oxide preparation and support materials, is applicable also in the case of copper. It must be particularly emphasised, however, that the production of an active material is especially dependent on the temperature of reduction of the oxide. By lowering the temperature of reduction of a given sample of copper oxide from 200° C. to 150° C. a fivefold increase in the adsorptive capacity of the resultant copper for hydrogen was achieved and a corresponding increase in catalytic activity was secured [3]—an activity far superior to those recorded by Sabatier for copper catalysts. A temperature of 150° C. represents an impracticably low temperature of reduction of ignited copper oxide, the time required for reduction being several days, but a reduction temperature of 200° C. can be employed with quite good results. Thus, Pease [4] found that such a catalyst could be used to measure the rate of hydro-

[1] Kelber, *Ber.*, 1924, **57**, 136, 142.
[2] Kahlenberg and Ritter, *J. Physical Chem.*, 1921, **25**, 89.
[3] Taylor, *Colloid Symposium*, Madison, Wisconsin, 1923.
[4] *J. Amer. Chem. Soc.*, 1923, **45**, 1196.

genation of ethylene at 0° C. The sensitivity of the product to the reduction of temperature is probably to be ascribed to the exothermicity of the reaction. Slow rates of hydrogen gas passage are therefore to be recommended. It is a good plan to initiate reduction of copper oxide at a temperature 50 degrees above the chosen reduction temperature, and, after the process has started, to lower the temperature to that chosen. Considerable economy of time is thereby secured, as reduction occurs more rapidly at copper-copper oxide interfaces.[1]

Catalysts so prepared are useful only for reactions occurring below the reduction temperature. Brown and Henke [2] found that a copper catalyst prepared by ignition of the nitrate at 415° C. and reduction at 314° C. was efficient in the reduction of nitrobenzene about 260° C., but deteriorated rapidly. They found, however, that a catalyst prepared from the nitrate by precipitation of the oxide with sodium hydroxide was more robust and less sensitive to temperature—a fact recorded earlier by Sabatier. Apparently the product is a promoted catalyst owing its ruggedness to traces of adsorbed alkali remaining in the material. Some investigations of promoted copper catalysts should be made. Rideal and Hurst have shown [3] that copper-0·2 per cent palladium catalysts are superior to copper in the preferential combustion of carbon monoxide in hydrogen-oxygen mixtures. Brown and Henke state that small amounts of iron in the copper oxide are beneficial. Brown and Henke also studied supported copper catalysts, using pumice and asbestos. For short periods in the reduction of nitrobenzene, pumice was the better, and both were better than straight copper. For long runs the copper-asbestos was superior.

Iron and cobalt.—Complete reduction of the oxides of these metals can only be readily accomplished at much higher temperatures than are employed in the case of nickel and copper oxides. Consequently the catalysts show much greater tendency to sinter. It is therefore to be recommended that these catalysts be used on a support material or admixed with a promoter. Alkalis, ceria, thoria, and alumina have been used for promoted iron catalysts with good success.

Calcination of cobalt nitrate can be conducted at 400°-450° C. Reduction of the oxide at 400° C. for four hours gives an active catalyst which still contains large quantities of oxide. Reduction at 600°-700° is necessary for complete reduction of the oxide. A supported cobalt oxide can be reduced with safety in the temperature region of 450°-500° C. The reduction of iron oxide at 400°-450° C. is slow, but an active catalyst is obtained even when considerable amounts of oxide still remain in the contact mass.

Platinum.—Unsupported platinum catalysts may be obtained in the form of platinum sponge, platinum black, prepared by two different methods, and as colloidal platinum. Platinum sponge is prepared by

[1] Pease and Taylor, *J. Amer. Chem. Soc.*, 1921, **43**, 2179.
[2] *Loc. cit.* [3] *J. Chem. Soc.*, 1923, **123**, 696.

gentle ignition of ammonium chloroplatinate and is the least active of the three forms.

A variety of methods of preparation of platinum black have been suggested. One method is essentially that of Loew [1] and of Mond, Ramsay, and Shields,[2] which consists in the reduction of a dilute solution of chloroplatinic acid by a solution of sodium formate, followed by a thorough washing of the precipitated platinum. A modification of this method employed by Willstätter and Waldschmidt Leitz [3] has been tested thoroughly and found to give excellent results.

Adams and Voorhees [4] claim that a much more active platinum black than that prepared by Loew's method is obtained by fusing chloroplatinic acid with an excess of sodium nitrate. When the cooled melt is washed with water, a brown oxide is obtained which turns black during the actual hydrogenation. Adams and Voorhees think that this is a black platinum oxide which loses much of its activity if complete reduction to platinum occurs, since the catalyst which has lost its activity may be revivified by shaking a short time with air. Adams and Carrothers [5] have found that in the hydrogenation of aldehydes the activity of catalysts so prepared is greatly increased by the presence of ferrous salts in the reaction system. An optimum concentration of 0·0001 mol. of ferrous salt per 100 c.c. of aldehyde reaction mixture was obtained.

Colloidal sol catalysts.—Colloidal sols of the metals platinum and palladium, dispersed in various solvents such as water, alcohols, acetic acid, or hydrocarbons, are now generally employed for the saturation of unsaturated organic substances in the organic chemical laboratories. The simple sols prepared by electric dispersion methods or from the double chlorides by reduction to metal, with hydrazine, hydroxylamine, or formaldehyde, are too sensitive to coagulation and precipitation by electrolytes to render them of any great utility, and, in consequence, protected sols are generally employed. Paal [6] first employed as protective agents two degradation products of egg-albumin, protalbinic and lysalbinic acid.[7] Albumin is gently hydrolysed with caustic soda and the protalbinic acid precipitated by the addition of sulphuric acid to the point of neutrality. The filtrate is evaporated to a small bulk, acidified, and the lysalbinic acid precipitated is purified by dialysis. In order to prepare an active platinum or palladium catalyst a dilute solution of a salt of these metals is added to a solution of the sodium salt of the protalbinic or lysalbinic acid, the metal salt being precipitated from solution. The platinum protalbinate is dissolved in the smallest possible amount of caustic soda, the solution diluted with water and purified, as far as possible, from excess

[1] *Ber.*, 1900, **23**, 289. [2] *Phil. Trans.*, 1895, **186A**, 657. [3] *Ber.*, 1921, **54**, 113.
[4] *J. Amer. Chem. Soc.*, 1922, **44**, 1397.
[5] *J. Amer. Chem. Soc.*, 1923, **45**, 1071. See also *ibid.*, 1924, **46**, 1675; 1925, **47**, 1047.
[6] *Ber.*, 1904, **37**, 124; 1905, **38**, 1398; 1908, **41**, 2273; 1909, **42**, 2239.
[7] *Ibid.*, 1902, **35**, 2195.

lkali by dialysis. On warming the solution with a few drops of ydrazine or formaldehyde a stable sol is readily obtained.

Skita [1] suggested the protective colloid, gum arabic, as a sub-itute for the protalbinic and lysalbinic acids of Paal. Since the gold umbers or protective powers of these protective colloids are prac-cally identical,[2] platinum and palladium protected by gum arabic re generally employed, being more readily prepared than Paal's roducts. Other protective colloids which may be employed are elatine and occasionally dextrine or starch. The two factors to be onsidered in the preparation of such protected catalytic sols are tability and efficiency. The stability will be dependent on the degree f protection afforded by the colloid, most readily determined by the old numbers. For example, for the above-mentioned protective olloids the gold numbers with gelatine as standard are

Colloid.	Gold Numbers.
Gelatine . . .	100
Albumin . . .	20
Dextrine . . .	0·66
Starch	0·40

he efficiency of the catalyst will evidently depend upon the dispersion nd the extent of active surface. The addition of a protective colloid o a disperse platinum sol results in the diminution of the active surface nd an increase in the stability. The inhibitive influence of protective olloids on catalytic processes was first demonstrated by Groh [3] and xamined in more detail by Rideal [4] and Iredale.[5] Iredale confirmed ie data of Groh that protective colloids cut down the catalytic activity the sol, the inhibitive numbers of the various colloids being approxi-ately the same as the gold numbers, whilst Rideal showed that there isted an optimum concentration when gum arabic was employed as rotective colloid, the colloid being added before reduction of the etal salt, being 2 milligrms. of gum for every 10 milligrms. of atinum or 5 milligrms. of palladium. Rocosolano [6] obtained data protecting a platinum sol prepared by Bredig's method with arious protection agents, which confirm Iredale's observations.

If but a small amount of protection agent be employed, not all of e amicrons of the metal sol will be protected, and, on the addition of electrolyte, these unprotected particles will coagulate with a resulting crease in catalytic activity. Increase in the protective colloid con-ntration will effect a peptisation or redispersion of these. Evidently e optimum concentration of colloid is such that the sol is prepared as disperse form as possible, but protected to the smallest extent mpatible with stability in presence of the reactants. It may be noted

[1] *Ber.*, 1911, **44**, 2862; 1912, **45**, 1627.
[2] Gortner, *J. Amer. Chem. Soc.*, 1920, **42**, 595.
[3] *Zeitsch. physikal. Chem.*, 1914, **88**, 419.
[4] *J. Amer. Chem. Soc.*, 1920, **42**, 749.
[5] *J. Chem. Soc.*, 1921, **49**, 109.
[6] *Compt. rend.*, 1921, **173**, 41, 234.

that a concentration of one part of gelatine in a million of water may just be detected by this method of catalytic inhibition. If Bredig's electric arc platinum be employed, the sol is relatively coarser than that prepared by the reduction of a soluble platinum salt in solution, and consequently the dispersive or peptising influence of the protective colloid is not so marked.

A protected colloidal sol formed by the dispersion of an intimate mixture of the metals from a solution of the mixed salts is more effective both in respect to stability and efficiency than an equivalent sol of either of the pure metals. This is indicated by the following approximate times for half completion of the hydrogenation of equal weights of sodium phenyl propiolate in solution :[1]

Composition of Catalyst.		Time of Half Completion. Minutes.
Milligrms. Pd.	Milligrms. Pt.	
10	0	7·0
5	5	5·0
1	9	11·0
0·2	9·8	7·0
0·1	9·9	12·0
0·01	9·99	30·0
0	10	39·0

Hydrogenation in the presence of metallic catalysts may conveniently be classified, according to Sabatier,[2] in three groups :

(1) Reductions with simultaneous fixation of hydrogen.
(2) Fixation of hydrogen by unsaturated compounds.
(3) Hydrogenation with accompanying rupture of the molecule.

A résumé of the typical examples of these three groups, as cited by Sabatier, is given in the following, together with a fuller description of those reactions having a more technical significance.

Reductions with Simultaneous Fixation of Hydrogen

Oxides of nitrogen.—Nitric oxide is readily reduced in presence of nickel at 180° with formation of ammonia and water, the equation being

$$2NO + 5H_2 \longrightarrow 2NH_3 + 2H_2O.$$

The ammonia formed has a tendency to combine with unchanged nitric oxide to form nitrogen and water :[3]

$$4NH_3 + 6NO \longrightarrow 5N_2 + 6H_2O.$$

This reaction is of importance in the process, elsewhere discussed

[1] Rideal, *Trans. Farad. Soc.*, 1923, **19**, 1.
[2] *La Catalyse en chimie organique*, 1913.
[3] Sabatier and Senderens, *Compt. rend.*, 1902, **135**, 278.

(p. 169), of ammonia oxidation, as its occurrence in that process may diminish considerably the efficiency of such catalytic oxidation.

Nitrogen peroxide is reduced by hydrogen in presence of nickel at 180°. The ammonia formed interacts with unreduced oxides, and ammonium nitrite and nitrate are produced. Further hydrogenation yields ammonia and water :

$$2NO_2 + 7H_2 \longrightarrow 2NH_3 + 4H_2O.$$

With high concentrations of nitrogen peroxide the reaction is very energetic, producing incandescence in the neighbourhood of the contact mass and frequently giving rise to explosions.

Similarly with the vapours of nitric acid, at 200° ammonium nitrate is produced, whilst at 350° nitrogen, ammonia, and water are the reaction products.

Organic nitro-compounds.—The aliphatic nitro-compounds are readily hydrogenated with nickel to the corresponding amine,

$$RNO_2 + 3H_2 \longrightarrow RNH_2 + 2H_2O,$$

but at more elevated temperatures the hydrogenation may proceed still further. Thus, nitromethane yields methylamine, but may partially yield methane and ammonia : [1]

$$CH_3NO_2 + 4H_2 \longrightarrow CH_4 + NH_3 + 2H_2O.$$

Similarly, aromatic nitro-compounds yield the corresponding amines. Further hydrogenation at higher temperatures yields the aromatic hydrocarbons and ammonia, whilst more elevated temperatures of reaction may carry the hydrogenation of the aromatic hydrocarbon yet further, yielding methane. Thus, in successive stages, nitrobenzene will yield aniline and water, then benzene, ammonia, and water, and with complete hydrogenation methane, ammonia, and water. By controlling the temperature the two latter reactions may be practically suppressed, and good conversion of nitrobenzene to aniline obtained.[2]

Aniline.—The vapour-phase reduction of nitrobenzene in presence of contact agents has been exhaustively studied by Brown and Henke.[3] They find that with nickel, and with cobalt containing small amounts of nickel, the reduction proceeds beyond the aniline stage, benzene and ammonia, and even methane and ammonia, being produced. With carefully controlled conditions, however, 95 per cent yields of aniline could be obtained. No azoxybenzene or azobenzene is produced. With copper and silver there is no reaction beyond the aniline stage, nor is azoxybenzene nor azobenzene produced. Copper shows a great tendency to sinter, however, with use; it should be prepared with an added promoter if its life is to be prolonged. Lead and bismuth seem to be the best catalysts if it is desired to stop the reduction at the

[1] *Compt. rend.*, 1902, **135**, 226. [2] Senderens, F.P. 312615/1901.
[3] *J. Physical Chem.*, 1922, **26**, 161, 272, 324, 631, 715; 1923, **27**, 52.

azoxybenzene or azobenzene stages. The yields of these partially reduced products progressively decrease as the catalyst is used. This appears to be due to oxidation of the catalyst metal, and the activity may be restored in part by reduction in hydrogen. Thallium gave a 90 per cent yield of azobenzene at 260°, but the activity diminishes rapidly, probably owing to the metal melting. Antimony, manganese, and chromium were found to have some catalytic activity, and the same was true of the lower oxides of molybdenum, vanadium, uranium, cerium, and tungsten, the first two being the most efficient in this group. Alumina showed a little activity, but commercial tellurium and the oxides of calcium, barium, and silicon showed none.

More recently [1] the same authors have shown that tin is an excellent catalyst for the reduction of nitrobenzene to aniline. It is superior to copper at most rates of gas passage. It is superior to nickel at all but the highest rates tried. The catalyst is best prepared from the hydroxide by precipitation with sodium carbonate from a stannous chloride solution. Oxidation of the hydroxide prior to reduction increased the efficiency of the resulting catalyst, the lower the temperature of oxidation the better the resulting catalyst. The lower the temperature of reduction of the oxide the better was the resulting catalyst. This catalyst is here mentioned in some detail because it is a new-comer in the ranks of reduction catalysts. It would be interesting to know whether it is a hydrogenation catalyst or whether its action depends on alternate oxidation and reduction of the catalyst.

On the technical side there is some evidence that vapour-phase hydrogenation has received serious consideration. The patents to Legge and Adam [2] indicate that a copper catalyst is very efficient, conducts heat well, and can be regenerated. Copper oxide is fused, cooled, and broken to size. Hydrogen or water gas in excess is mixed with the nitrobenzene. Quantitative yields are obtained at 230° C. The Badische Anilin- und Soda-Fabrik suggest [3] also a mixture of carbon monoxide, steam, and nitrobenzene with a copper catalyst. They claim also the use of promoters such as the oxides of the alkali metals, phosphates, silicates, tungstates. Brochet [4] has suggested the catalytic reduction of nitrobenzene in liquid media in presence of nickel.

The huge quantities of aniline which to-day are employed in the organic chemical industry are produced by the reduction of nitrobenzene. For industrial purposes practically exclusive use is made of the method due to Bechamp,[5] which consists in reduction of the nitro body using iron and acids. Acetic acid, the original acid employed by Bechamp, is replaced by the cheaper mineral acids. In the reaction, which is frequently formulated by the equation

$$C_6H_5NO_2 + 3Fe + 6HCl = C_6H_5NH_2 + 2H_2O + 3FeCl_2,$$

[1] *J. Physical Chem.*, 1923, **27**, 736.
[2] B.P. 166249 and 166283.
[3] F.P. 511256.
[4] B.P. 16936 and 22523/1913.
[5] *Ann. Chim.* [3], 1854, **42**, 186.

is found that much smaller amounts of acid than correspond to the oichiometric relationships are required. Indeed, hydrochloric acid to ne extent of 3 per cent of the theoretical requirements is found to be dequate; in certain cases ferrous chloride to an equivalent amount substituted for this hydrochloric acid and, in presence of iron and ater, a clean reduction of the nitrobenzene occurs. It is therefore bvious that, in this case, it is not a question of simple reduction by eans of hydrogen. The operation as conducted shows catalytic atures. No single explanation of the mechanism of the process as et finds general acceptance. According to Witt [1] the ferrous chloride converted by the reduction process to an oxychloride, which then teracts with the iron to regenerate ferrous chloride and to give simul-neously magnetic oxide of iron, Fe_3O_4:

$$6FeCl_2 + C_6H_5NO_2 + H_2O \longrightarrow 3FeOCl_4 + C_6H_5NH_2,$$
$$4FeOCl_4 + Fe \longrightarrow FeCl_2 + Fe_3O_4.$$

he sum-total of the reaction could then be expressed by the equation

$$4C_6H_5NO_2 + 9Fe + 4H_2O \xrightarrow{FeCl_2} 4C_6H_5NH_2 + 3Fe_3O_4.$$

ccording to Wohl [2] the finely divided iron in conjunction with water rms the reducing agent

$$C_6H_5NO_2 + 2Fe + 4H_2O \longrightarrow C_6H_5NH_2 + 2Fe(OH)_3.$$

ohl assumes that the ferric hydroxide interacts with ferrous chloride give a double salt which, by further action of metallic iron, is con-erted to ferrous chloride and magnetic oxide. It will be recalled, owever, in this connection that, in the Bergius process, water and on react at 300° to yield hydrogen under high pressures when acids salts, *e.g.* ferrous chloride, are employed as catalyst. It is possible at, under the conditions prevailing in this reaction, due to the presence a hydrogen "acceptor", nitrobenzene, the reaction proceeds at the wer temperature. The real reducing agent would then be hydrogen om the interaction of water and finely divided iron.

With other acids than hydrochloric acid the same circumstances ld. A small percentage of the theoretical hydrogen requirements are fficient for the conduct of the process. Furthermore, the method is t restricted to this particular nitro-compound. The reaction is nerally applicable and is utilised in the organic dye-stuff industry in merous cases with which it is beyond the scope of this volume to deal.

Dinitro-derivatives yield the corresponding diamines. Nitrophenols eld aminophenols with side reactions yielding ammonia, phenol, and ater, and some aniline. Nitrous ethers yield the corresponding nines by reduction in presence of nickel, just as do the isomeric tro-compounds. A production of the secondary and tertiary amines

[1] *J. Soc. Chem. Ind.*, 1887, 218. [2] *Ber.*, 1894, 27, 1436, 1817.

always occurs, the secondary amine generally being produced in the greatest amount. Gaudion [1] explains his results with these compounds by assuming isomerisation of the nitrous ethers in presence of the catalyst.

Oximes on catalytic reduction yield primary and secondary amines. The amides of the fatty acids yield the corresponding primary amine and water with some formation of the secondary amine by rupture of the molecule and simultaneous production of ammonia.

Halogen derivatives.—Direct reduction of halogen aromatic compounds is possible, employing finely divided nickel as catalyst. The ease of reduction is a function of the compound. The presence in the ring of substituent groups such as methyl or hydroxy-radicals facilitates reduction. In general, the chloro-derivatives are the most easily reduced. The bromo-derivatives are less easily reduced, and the iodo-compounds least of all. This order is what would be expected in view of affinity relationships between hydrogen and the respective halogens. On an intermediate compound theory of catalysis also the same order would be forecasted, since nickel chloride is readily reduced by hydrogen at 270°; whereas the bromide is less easily reduced and the iodide practically not at all at such temperatures.

In exemplification of the catalytic reduction the following reactions will serve. At 270° monochlorobenzene is rapidly hydrogenated, benzene being formed. A certain quantity of diphenyl is, however, simultaneously produced, due possibly to the direct action of the metallic catalyst on the chloro-derivative.

Poly-chloro-derivatives yield the reduced products in successive stages. Thus dichlorobenzene gives successively mono-chlorobenzene and benzene. From hexachlorobenzene a mixture of the tri-, di-, and mono-chlorobenzenes is obtained.

The chlorotoluenes are more readily reduced than the chlorobenzenes. Trichlorophenol gives a mixture of 70 per cent of phenol and some monochlorophenols. Chloroanilines readily yield the corresponding hydrochloride. Chloronitro-compounds suffering simultaneous reduction of the chlorine and nitro-groups also yield the hydrochlorides of the corresponding amine.

Oxygen-containing carbon compounds.—A number of oxygen-containing carbon compounds may be catalytically reduced with simultaneous fixation of the hydrogen. Thus, ethyl acetoacetate is converted to ethyl butyrate according to the equation

$$CH_3 . CO . CH_2 . COO . C_2H_5 + 2H_2 \longrightarrow CH_3 . CH_2 . CH_2 . COO . C_2H_5 + H_2O.$$

This reaction is always accompanied by side reactions. A split of the molecule may occur ($CH_3 . CO . CH_2$–and–$COO . C_2H_5$), the products yielding further reduced substances, the former acetone and secondary

[1] *Ann. Chim. Phys.*, 1912 (viii.), **25**, 129.

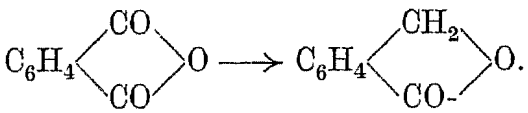
propyl alcohol. the latter ethyl formate, which decomposes under the reaction conditions to ethyl alcohol and carbon monoxide. This latter may be transformed to methane during the reaction. Alternatively, condensation of the molecule may occur as a side reaction, catalytically assisted by the nickel. The hydrogen does not function in the change, the products of condensation being dehydracetic acid and ethyl alcohol, according to the equation

$$2(CH_3 . CO . CH_2 . COO . C_2H_5) = (CH_2 . CO)_4 + 2C_2H_5 . OH.$$

With nickel of medium activity aromatic ketones are reduced to the corresponding benzene derivative. Thus, acetophenone, $C_6H_5 . CO . CH_3$, yields ethyl benzene. Similarly, aromatic diketones give the corresponding hydrocarbons :

$$C_6H_5 . CO . CO . C_6H_5 + 4H_2 \longrightarrow C_6H_5 . CH_2 . CH_2 . C_6H_5 + 2H_2O.$$

The anhydrides of dibasic acids give the corresponding lactones. Thus succinic anhydride gives butyrolactone, orthophthalic anhydride the corresponding phthalide, *e.g.*



The phenols and poly-phenols may be reduced to the corresponding hydrocarbons, but the yields are low.

Aldehydes.—Aldehydes on reduction are converted to the corresponding alcohols :

$$R . CHO + H_2 = R . CH_2 . OH.$$

This reaction is of prime importance in the modern work on the production of synthetic alcohol. As shown elsewhere (p. 316), from calcium carbide as starting-point, acetaldehyde may be synthesised, via acetylene, which is catalytically hydrated to yield the aldehyde. Using Sabatier's catalytic hydrogenation process, the aldehyde thus produced may be converted to ethyl alcohol. The reaction is conducted in the presence of reduced nickel at 140°, using dry aldehyde vapour and pure hydrogen. The completeness of the synthesis is limited by the reverse process of dehydrogenation of the alcohol produced, but, with careful control, a conversion of 80 per cent of the aldehyde is possible in a single passage over the catalyst. Temperature control must also be rigorous owing to the possibility of catalytic decomposition of the aldehyde, which, at 180°, under these conditions is rapidly converted to methane and carbon monoxide,

$$CH_3 . CHO = CH_4 + CO.$$

The products of reaction, consisting of alcohol, unchanged acetaldehyde, and hydrogen, are collected, and, by a process of continuous fractiona-

tion, are separated, the unchanged materials returning to the reaction system.

Armstrong and Hilditch [1] have shown that the reduction occurs more slowly than the hydrogenation of simple ethylenic compounds, but the mechanism is the same.[2] Water vapour inhibits the hydrogenation process markedly. The Lonza Electrizitäts Werke carry out the process technically by using a large excess of hydrogen, which is stripped of reaction product and returned to the inlet of the system.

Oxides of carbon.—Both carbon monoxide and carbon dioxide may be reduced by hydrogen in the presence of metallic nickel. In each case the products of reduction are methane and water, the reactions occurring being representable by the equations

$$CO + 3H_2 = CH_4 + H_2O,$$
$$CO_2 + 4H_2 = CH_4 + 2H_2O.$$

With an active nickel catalyst the reaction with carbon monoxide may commence as low as 180° - 200°, the velocity of reaction increasing rapidly with the temperature, so that at 250° the conversion is practically complete. With carbon dioxide the reaction commences at a somewhat higher temperature, towards 230°, and is rapid above 300°. It has been suggested that the dioxide may thus be used as a suitable starting-point for the preparation of pure methane. It is necessary, however, to exercise care in the process, otherwise carbon monoxide will be found in the reaction product after removal of the carbon dioxide by alkali. The occurrence of carbon monoxide in the hydrogenated products of carbon dioxide is of interest, and further study of this point should yield information on the precise mechanism of reduction.

With carbon monoxide at temperatures above 250° a second reaction may occur, also catalytically assisted by metallic nickel, as well as by many metallic catalysts, *e.g.* iron. Carbon monoxide is decomposed, yielding carbon and carbon dioxide according to the equation

$$2CO \rightleftarrows C + CO_2.$$

The carbon is deposited on the nickel catalyst, rapidly rendering it ineffective catalytically.

The technical application of these hydrogenation processes to the production of illuminating gas has been the object of considerable investigation. A review of this work may therefore here be given.

Technical production of methane.—Elworthy in 1902 [3] was the first to apply the process of Sabatier and Senderens to the technical production of methane from carbon monoxide. He employed water gas as the source of his methane. The gas was freed from carbon dioxide and so much hydrogen added that the theoretical mixture ($CO + 3H_2$)

[1] *Proc. Roy. Soc.*, 1920, **97A**, 259. [2] See p. 137. [3] B.P. 12461/1902 and 14333/1904.

for methane formation was obtained. The conversion was to be effected by passage of the gases over finely divided nickel at 250°. The process was to be exploited by an English company, but technical difficulties, mainly the short life of the catalyst coupled with the death of the patentee, affected the progress of the work adversely, and the problem therefore remained unsolved.

Sabatier himself attempted the solution of the problem.[1] At the outset he sought to reduce carbon dioxide by means of hydrogen at temperatures of 350°. Later he proposed an alternative process,[2] utilising the decomposition of carbon monoxide to carbon and carbon dioxide which occurs readily at 500° in the presence of a nickel catalyst, together with the observation that the carbon deposited in the mass readily combines with superheated steam to form carbon dioxide and methane. In this manner mixtures of methane, hydrogen, and carbon dioxide could be produced from water gas. The reaction could be conducted in the two stages or, by passage of suitable proportions of water gas and superheated steam simultaneously over the catalyst at 500°, the two reactions could be superimposed. In conjunction with A. Girard, considerable energy was expended in attempting this alternative scheme on economic lines, but presumably without success.

In a later patent[3] Sabatier returned to the direct reduction process, employing a low-temperature water gas with a high-carbon dioxide content and a correspondingly low content of carbon monoxide (12 per cent). In this way the necessary excess of hydrogen was obtained. The gas, after removal of the carbon dioxide, was passed first over heated copper to remove impurities, and then over the nickel catalyst to convert the mixture into methane and hydrogen.

An alternative method of producing the hydrogen-rich gas necessary for the production of methane was worked out by Bedford in the laboratories of Prof. Erdmann, Halle-a.-S., and the technical possibilities of the process were exploited by the Cedford Gas Process Co. in England.

The difficulties in the way of a technical solution of the problem of reduction of carbon monoxide by hydrogen in the presence of nickel may be briefly summarised as follows:

(1) Theoretically, three volumes of hydrogen are required for one of carbon monoxide. In technical practice, it is found that at least five volumes are requisite.

(2) Sulphur-containing gases poison the nickel catalyst.

(3) The decomposition of carbon monoxide to carbon dioxide and carbon may occur with decomposition of the latter on the nickel catalyst resulting in loss of catalytic activity.

The use of low-temperature water gas, as suggested by Sabatier, to overcome the first difficulty suffers from the disadvantage that considerable quantities of carbon dioxide must be removed, an operation of considerable expense. Alternatively, Elworthy's proposal to admix

[1] F.P. 354621/1905. [2] F.P. 355900/1905. [3] F.P. 400656/1908.

hydrogen is limited in its application by the relatively high cost of hydrogen. The attainment of the hydrogen-rich gas can, however, be realised by removal of carbon monoxide from water gas, and this is possible by the physical method of liquefaction, making use of the difference in the boiling points of the two constituents ($H_2 = -252{\cdot}5°$; $CO = -190°$). As mentioned elsewhere (see p. 228), this process of liquefaction has been employed by Frank and Caro for the preparation of hydrogen.

By a modification of the method of operation it was found possible so to conduct the liquefaction that at the temperature of liquid air so much carbon monoxide was removed from water gas that an uncondensed fraction containing 14 per cent of carbon monoxide was obtained. The liquefied carbon monoxide was vaporised, a portion mixed with the 14 per cent fraction to bring it up in composition to 17 per cent, and the remainder burned in gas-engines to yield motive power to drive the compressors and also to work the pumps necessary to remove all traces of carbon dioxide from the original water gas. This was accomplished by washing with water and with alkali under pressure, or, according to the patent of Behrens and Behrens,[1] by alcohol under pressure in a circulatory system.

The adoption of the liquefaction process to obtain the hydrogen-rich gas mixture simultaneously solved the second difficulty in the process. For, in the cooling operation, it was found that all sulphur compounds were completely removed from the uncondensed portion and remained behind as solids in the carbon monoxide-rich fraction. A gas was obtained so free from sulphur impurities that after the passage of 500,000 litres over 200 grms. of reduced nickel the activity of the catalyst was absolutely unimpaired. From other sources it is possible to confirm this observation as to freedom from sulphur, and it may be stated that as much as 3,000,000 volumes of gas per volume of catalyst may be successfully treated without recording a departure from the quantitative nature of the conversion.

The further difficulty associated with the process, due to carbon deposition, is practically eliminated by use of the gas with 5 volumes of hydrogen to 1 of carbon monoxide. The diluent effect of the hydrogen is sufficiently great to prevent decomposition occurring in any marked degree.

For the reduction process it was found that three quartz tubes,[2] 1·5 metres long and 12 cm. diameter, each containing 200 grms. of finely divided nickel, were adequate for the treatment of 400-500 cubic feet of gas per hour. The yield of methane-rich gas thus obtained averaged 200-250 cubic feet per hour. The quartz tubes were maintained at a temperature of 280°-300°. Since the reaction is strongly exothermic,

$$CO + 3H_2 = CH_4 + H_2O + 48{,}900 \text{ cals.},$$

[1] D.R.P. 226942.

[2] Thermal Syndicate, Wallsend.

may readily be shown that with a gas of 17 per cent carbon monoxide ontent the process will maintain itself without the supply of external eat.

In a sixty-hour test run under these conditions the following sample ata were collected :

	CO_2.	CO.	H_2.	N_2.	CH_4.	Cal. Val. per cub. ft.
(*a*) Composition of the water gas .	3·8	38·3	52·2	5·7	—	288
(*b*) Water gas freed from CO_2 .	0	41·0	54·0	5·0	—	—
(*c*) Hydrogen-rich gas . .	0	13·9	84·3	1·8	—	298
(*d*) Carbon monoxide-rich gas .	0	93·2	0·5	6·3	—	325
(*e*) Mixture of (*c*) and (*d*) used for reaction	0	16·3	80·9	2·8	—	298
(*f*) Samples after reduction . (1)	0	0	64·8	6·9	28·3	466
(2)	1·4	0·2	60·6	5·8	31·8	488
(3)	0·6	0	61·4	6·2	31·8	490

It was shown that if diminution in activity of the nickel due to arbon deposition occurred, this could be removed by slowing down he stream of gas for a period of time during which the nickel recovered s activity. According to Mayer and Henseling,[1] this is due to inter- ction of the deposited carbon with hydrogen to form methane.

To avoid carbon deposition, the carbon monoxide content is kept elow 17 per cent. Hence a gas with more than 32 per cent of methane annot be obtained in one operation. Actually, however, by addition f further quantities of carbon monoxide to the reduced gas, the process ay be repeated and a gas containing as much as 76 per cent of methane ay be obtained by successive treatments.

As to the economics of the process, Mayer and Henseling are essimistic. Erdmann, on the other hand, claims considerable pos- bilities for the process. It is obvious that a considerable reduction volume occurs in the process, so that large volumes of gas must ecessarily be treated to obtain a given output. This would militate gainst its successful utilisation as a source of illuminating gas *per se*. n the other hand, the considerable increase in calorific value per nit volume accompanying the conversion suggest its application as n enriching agent for water gas produced in gas-works for addition the ordinary coal gas supply. This would obviate the use of oil upplies for carburetting water gas and therefore increase the quantities f such material available for other purposes. There seems to be istinct possibilities of use for a gas with a calorific value averaging 50 B.T.U. capable of production at a figure comparable with that of oal gas. The product of the Cedford process, it was seen, averages 30 B.T.U. per cubic foot, so that admixture of this with an ordinary

[1] *J. f. Gasbeleucht.*, 1909, **52**, 169, 197.

water gas of 300 B.T.U. in equal proportions would yield a gas of calorific value well above the 350 B.T.U. standard. The cost of production, also, should be within the limits of practical consideration. Nevertheless, so far as is known, no considerable technical development has taken place in such direction. Extended familiarity with technical catalytic processes may, however, promote such development along the lines suggested by the above outline or in similar directions, employing other catalytic agents for the production of the methane.

Medsforth [1] has shown that this reaction can be much more rapidly conducted if the nickel catalyst contains a promoter. Ceria, thoria, glucina, chromium oxide, alumina, and silica gave a from 17-fold to 12-fold increase in velocity over that obtainable with the straight nickel catalyst. Zirconia, molybdenum, and vanadium oxides were somewhat less efficient, though still good promoters. Tin and magnesium oxides, copper and silver metals produced no acceleration over the straight nickel. With the carbon dioxide reaction the increases in velocity were somewhat less than those recorded for the monoxide reaction, although the order of efficiency was the same. The mechanism of the promoter action has already been discussed.[2]

Armstrong and Hilditch [3] conclude that when purified water gas is passed over nickel at 200°-300° C. the predominating reaction is

$$2CO + 2H_2 = CO_2 + CH_4.$$

The reaction is regarded as the sum of two reactions:

$$2CO + 2H_2O = 2CO_2 + 2H_2,$$
$$CO_2 + 2H_2 + 2H_2 = CH_4 + 2H_2O,$$

the former of which is regarded as occurring in the same manner as the reaction in presence of copper previously studied by them,[4] namely, via formic acid:

$$CO + H_2O \longrightarrow HCOOH \longrightarrow CO_2 + H_2.$$

With cobalt the reaction commences at a lower temperature, 180° C., but the reaction yielding carbon dioxide and methane is subsidiary to the main methanation process:

$$CO + 3H_2 = CH_4 + H_2O.$$

Silver is inert, iron almost so, platinum and palladium of minor activity. Increase of pressure up to 6 atmospheres increased the minimum temperature of interaction. The reaction producing carbon dioxide and methane produces more methane from water gas than any other reactions. It may therefore have value as a means of increasing the methane content or lowering the carbon monoxide content of town's gas.

[1] *J. Chem. Soc.*, 1923, **123**, 1452.
[2] Chapter V. p. 104.
[3] *Proc. Roy. Soc.*, 1923, **103A**, 25.
[4] *Proc. Roy. Soc.*, 1920, **97A**, 265.

Various efforts to produce methane from carbon monoxide and hydrogen in the presence of metallic copper have thus far proved unsuccessful. This raises an interesting problem as to the reasons why nickel and copper are thus differentiated.

Partial reduction of carbon monoxide.—The possibilities inherent in a process for the conversion of water gas into methyl alcohol according to the reaction

$$CO + 2H_2 \longrightarrow CH_3OH$$

first attracted the attention of Sabatier and Senderens.[1] They found, however, that with nickel as a catalyst no trace of alcohol was obtained, the reaction proceeding entirely to methane:

$$CO + 3H_2 \longrightarrow CH_4 + H_2O.$$

At a later date [2] the Badische Co. claimed the utilisation of pressure in a process for the conversion of blue water gas into a mixture of oils. Pressures over 100 atmospheres and a temperature range of 360°-420° C. were claimed as suitable with catalysts consisting chiefly of metals, especially iron and others of the iron group, impregnated with alkalis; in addition zinc and zinc oxide were suggested as catalysts. The oils so produced consisted in part of hydrocarbons; the rest was water-soluble containing alcohols, acids, aldehydes, and ketones.

A paper patent in 1916 [3] describes the preparation of methyl alcohol from water gas at atmospheric pressures, utilising nickel or platinum as catalyst. In 1921 Calvert [4] claimed an 80 per cent conversion into methyl alcohol at atmospheric pressure. No details of the catalyst are given, but it was in all probability a metallic oxide. Patart [5] in the same year claimed the conversion of a gas mixture of composition corresponding to $2H_2 : CO$ at 300°-600° C. and at high pressures into methyl alcohol, utilising metals or oxides which are hydrogenating catalysts.

In 1923 the Badische patents appeared, and the technical plant at Merseburg was put into operation for the manufacture of pure methyl alcohol, whilst experiments on the production of long chain compounds, including alcohols and acids and hydrocarbons suitable for motor fuels, were continued by Fischer.[6] This phase of the process is at present just emerging from the experimental to the industrial stage.

It is clear that two stages in the process of reduction are distinct from one another, the primary or ready production of methyl alcohol, which is apparently followed by further reactions building up the hydrocarbon chain.

Methyl alcohol production.—From the heats of formation of the various reactants the heat of reaction to form methyl alcohol from the

[1] *Ann. Chim. Phys.* (iv.), 1905, 418. [2] D.R.P. 293787/1913 and B.F. 468427/1914.
[3] Dreyfuss, B.F. 492154/1916. [4] *Chem. Age*, 1921. 5, 153. [5] B.F. 540343/1921.
[6] *Brennstoff Chemie*, September 15, 1923; July 1, 15, 1924.

ideal water gas $2H_2 : CO$ is found to be 27,000 cals., the reaction being exothermic:

$$CO + 2H_2 = CH_3OH + 27{,}000.$$

The values of the equilibrium constant at various temperatures may be obtained with the aid of the approximation equation of the Nernst heat theorem:

$$\log_{10} K = -\frac{Q}{4{\cdot}571\,T} + 1{\cdot}5\Sigma\nu \log T + \Sigma\nu C,$$

where C represents the chemical constants.

Inserting the values $Q = 27.000$, $C_{H_2} = 1{\cdot}60$, $C_{CO} = 3{\cdot}5$, $C_{CH_3OH} = 3{\cdot}5$, $\nu = 2$ we obtain the following values of K_p:

Temperature ° K . .	400	500	600	700	800	1000
$\text{Log}_{10} K_p = \left(K_p = \frac{(H_2)^2(CO)}{CH_3OH}\right)$	- 2·40	1·88	2·94	4·72	5·98	7·80

It is clear that it is most advantageous, as in the ammonia synthesis, to operate at as low a temperature as is possible compatible with catalytic efficiency.

The importance of operating at high pressures is likewise evident from the fact that the equilibrium is displaced towards the methyl alcohol side with increase in pressure proportionally to a much greater extent than in the ammonia synthesis.

Thus, at 600° K or 327° C. the equilibrium constant is *ca.* 10^3; if water gas containing equal quantities of hydrogen and carbon monoxide be brought to equilibrium with methyl alcohol at various pressures, the partial pressures of each constituent will be

Total Pressure In Atmospheres.	Partial Pressure, H_2.	Partial Pressure, CO.	Partial Pressure, CH_3OH.
1	0·5	0·5	$9{\cdot}5 \times 10^{-2}$ mm.
10·1	5	5	0·125 atm.
225	50	50	125 atm.

The choice of catalyst for the reaction was evidently limited by the fact that hydrogenation to methane had to be avoided. More hope was to be found in substances such as metallic hydroxides, which readily yielded formates on interaction with carbon monoxide. The study of the nature of the products of decomposition of metallic formates had been carried out by Gieben, Hofmann, and Goldschmidt, and whilst potassium formate yielded the oxalate and hydrogen on heating, zinc formate was found to give good yields of formaldehyde, methyl formate, and methyl alcohol.

The experiments of Patart, of the Service des Poudres Français, and of the Badische Co. showed conclusively that zinc oxide was in

act an excellent catalyst, being quite active at temperatures of 400°-420° C., pressures of from 150-250 atmospheres being employed.

The Badische Co. are said to be operating at temperatures as low as 250°-300° C., with a zinc oxide catalyst promoted with chromium oxide and at a pressure of 200 atmospheres.

In operating the process, as has been indicated, special attention has to be paid in purification of the ideal water-gas mixture $2H_2 : CO$, not only in respect to sulphur compounds, but in the elimination of all traces of hydrogenating catalysts such as iron and cobalt and especially nickel salts. The catalysts prepared from oxides of metals in different systems in the periodic table, with the most basic oxide in excess, must likewise be free from these impurities as well as from alkalis. Copper has proved the most suitable metal as catalyst container.

Synthesis of hydrocarbon chains.—Whilst the primary formation of methyl alcohol on the surface of the zinc oxide catalyst apparently proceeds smoothly through the formate, the subsequent production of long chain hydrocarbons and their oxy-derivatives appears to be more complicated. As efficient catalysts, oxides or iron impregnated with strong alkalis at 400°-420° C. and 150 atmospheres may be used. The resulting product contains relatively large quantities of isobutyl and higher alcohols up to C_9, isobutyric and higher acids up to C_9, isobutyric aldehyde and higher aldehydes, acetone and higher simple and mixed ketones, about 2 per cent of esters, 1 per cent of hydrocarbons, and a small quantity of waxy solid.

The mechanism of formation of these long chains can be interpreted in various ways. Since the combination of a hydrogenating catalyst and a strong alkali are required to effect catalysis, this suggests the following sequence of reactions :

(1) $CH_3OH + CO \longrightarrow CH_3COOH$ on the alkali,
(2) $CH_3COOH + H_2 \longrightarrow CH_3CHO$ on the hydrogenator,
(3) $CH_3CHO + H_2 \longrightarrow C_2H_5OH$ on the iron.

The process commences again with ethyl alcohol as reactant.

If this mixture be heated to 400° C. in an autoclave the alcohols and aldehydes are decomposed and a mixture of saturated and unsaturated hydrocarbons are obtained, a suggestive method for the formation of natural naphthenic petroleum from water gas.

Hydrogenation of Unsaturated Compounds

By far the greater number of catalytic hydrogenation processes may be classified in this grouping, and in the hardening of oils the utility of the process finds a practical application. Examples of hydrogenation of all types of unsaturated compounds may be given, including compounds containing the ethylene double bond, the acetylene triple bond, the triple and quadruple linkage between carbon and nitrogen,

the double bond between carbon and oxygen, the benzene nucleus, and various other unsaturated nuclei.

Ethylene.—The ethylene linkage is readily hydrogenated in the presence of metal catalysts. Thus, in the presence of nickel, ethylene itself is hydrogenated at temperatures as low as 30°, ethane being the product. The rate of reaction increases with temperature, and is very rapid in the temperature interval 130°-150°. If the temperature employed be too high, decomposition of the hydrocarbon, in other words, dehydrogenation, also sets in, with deposition of carbon and liberation of a mixture of ethane, methane, and hydrogen, the two latter in larger quantities the higher the temperature employed. This behaviour is quite general for all the ethylene hydrocarbons investigated. At the lower temperatures hydrogenation proceeds more or less quantitatively to the corresponding saturated compounds. At elevated temperatures decomposition sets in, with formation of simpler hydrocarbons and hydrogen together with carbon and a small proportion of complex liquid hydrocarbons.

Mechanism.—The best kinetic studies of the hydrogenation of ethylene have been made by Rideal [1] using a nickel catalyst and by Pease [2] with copper. Rideal used a relatively inert nickel catalyst produced on a strip of nickel foil. He studied the rate of reaction of the mixed gases, at relatively low partial pressures (0-200 millimetres), in varying ratios, over the temperature interval of 30°-200° C. He found that, in excess of hydrogen, the velocity is proportional to the pressure of ethylene, in excess of ethylene to the hydrogen partial pressure. Ethane acts as an inert diluent. An optimum temperature of reaction occurs at about 137° C. The reaction velocity is governed not only by the rate of impact of the reactants on the free spaces of the catalyst, but also by the length of life of the molecules on the surface. These contrary factors gave a maximum velocity effect at 137° C. Rideal made the important observation that, on the most advantageous conditions of impact, the catalytic efficiency of his metal surface was only 0·04 per cent. Oxygen inhibits the reaction, hydrogenation of the ethylene being negligible before all the oxygen is converted to water. From his data, Rideal deduced a heat of adsorption of hydrogen by nickel of 12,000 cals., a surprisingly high value which was, however, subsequently confirmed by direct measurement.[3]

Pease showed that, in presence of copper, the bulk of the surface in contact with a stoichiometric mixture is largely covered by ethylene, and the rate of reaction is determined by the rate at which the hydrogen can reach active centres in the catalyst surface. Pease showed that the centres on the copper surface which are capable of

[1] *J. Chem. Soc.*, 1922, **121**, 309; see also Palmer, *Proc. Roy. Soc.*, 1921, **99A**, 402.

[2] *J. Amer. Chem. Soc.*, 1923, **45**, 1196, 2235; see also Grassi, *Il Nuovo Cim.*, 1016 (6), **11**, 147.

[3] Foresti, *Gazzetta*, 1923, **53**, 487; Beebe and Taylor, *J. Amer. Chem. Soc.*, 1924, **46**, 43.

adsorbing hydrogen were not all sufficiently active to produce hydrogenation, and that therefore, even in a very highly active catalyst (Pease's catalysts were so active that the reaction was rapid at 0° C.), the proportion of the surface which was catalytically efficient was a very small fraction of the total surface. This confirmation of Rideal's result in the case of nickel is of fundamental importance in the theory of contact catalytic change.[1]

The problem of hydrogenation of unsaturated hydrocarbons is allied to the experimental work of Bergius on the action of high-pressure hydrogen on coal and tar oils. Experimental investigation shows that, at 400° and 100 atmospheres hydrogen pressure, hydrocarbon oils result from coal, and that these yield, on distillation, products resembling the paraffin hydrocarbons. The application of catalytic agents to such reactions would seem to offer possibilities of development in a technical direction.

Alcohols with a single unsaturated linkage are hydrogenated, with formation of the corresponding saturated alcohol. Thus, at 130°-170°, in presence of nickel, allyl alcohol yields propyl alcohol. Similarly, citronellol,

$$(CH_3)_2C=CH(CH_2)_2 . CH(CH_3) - CH_2 . CH_2 . OH,$$

yields the dihydro-derivative.

With aldehydes, conversion to the saturated aldehyde is readily effected, but simultaneous reduction to the saturated alcohol occurs, though at a less rapid rate of reaction. Thus crotonaldehyde gives a 50 per cent yield of butyric aldehyde and 20 per cent of butyl alcohol when heated with hydrogen in presence of nickel at 125°.

By adjustment of the temperature of operation, ketones with ethylene linkages can be reduced to the saturated compound without simultaneous reduction of the ketonic grouping. Thus, at 160°-170°, phorone, $(CH_3)_2C=CH . CO . CH=C(CH_3)_2$, gives di-isobutyl acetone. At 225° the corresponding secondary alcohol and saturated hydrocarbon appear in the product.

Unsaturated acids are likewise hydrogenated without any action of the acid on the metal catalyst; this is of importance in the technical hydrogenation of oils, since these always contain small amounts of free acids.

The esters and glycerides of unsaturated acids are likewise hydrogenated readily in the vapour phase. For technical operation, however, the discovery that hydrogenation could be effected in the liquid phase obviated the necessity of employing the vapours of the oils, most of which are non-volatile. A considerable industry in the hydrogenation of oils has now been established, the details of which merit extended consideration.

[1] For further discussion see Poisons, Chapter VI. p. 127.

Hydrogenation of Oils

The classic studies of Sabatier and Senderens which have just been detailed undoubtedly laid the foundation for the development of the many processes now in technical operation for the hardening of oils by hydrogenation. The problem of oil hardening, briefly stated, consists in the conversion of oils which at the ordinary temperature are liquid into fats which are hard under the same conditions. Chemically expressed, the problem is the transformation, by addition of hydrogen to the molecule, of the glycerides of unsaturated acids, such as oleic acid, into the glycerides of the corresponding saturated acids, such as stearic acid. The hydrogenation is accompanied by the elevation of the melting point of the glyceride. Since the market value of solid or semi-solid fats is intrinsically higher than that of the liquid fats, it is obvious that such a transformation, if effected cheaply, has a large industrial importance in the soap, candle, and margarine industries.

Early efforts to effect hydrogenation of oils are almost legion, and all of them were failures technically. The early work of Chevreul and Berthelot is classic, many possible methods of introducing hydrogen being attempted. Chlorine,[1] bromine, and iodine[2] have all been proposed. Nascent hydrogen produced from finely divided zinc and water in the presence of olein under pressure was claimed by Tissier.[3] Schmidt's process of heating zinc chloride with oleic acid at 185° was tried, without success, upon a large scale. The process of Warentrapp, in which olein is fused with caustic potash with formation of palmitic acid, had an industrial application so long as the price of olein was low. The brisk advance in recent years of the price of this material has, however, destroyed the value of the process. The processes of Wilson and of Milly transformed oleic acid into oxystearic acid by the action of sulphuric acid. The losses in the process are, however, considerable and militate against its use. Hydrogen generated by electrolysis was also tried by Petersen, who electrolysed alcoholic solutions of oleic acid acidified with a mineral acid, nickel electrodes being employed. The yields obtained did not exceed 20 per cent. Aqueous fatty material acidified with sulphuric acid and electrolysed, as well as material previously sulphonated,[4] with subsequent electrolysis, have also been proposed as solutions of the problem. De Hemptinne employed the electric discharge upon a thin layer of oil in contact with hydrogen. Repeated operation thus gave yields up to 40 per cent.

Hydrogenation by catalytic action was shown by Sabatier and Senderens to be easy of accomplishment with bodies capable of vapor-

[1] Zurrer, D.R.P. 62407/1891; Imbert, U.S.P. 901905/1908.

[2] Goldschmidt, *Sitzungsber. K. Akad. Wiss. Wien*, 1875, **72**, 366; de Wilde and Geychler, *Bull. Soc. chim.*, 1889 (iii.), **1**, 295.

[3] F.P. 263158/1897.

[4] Waser, D.R.P. 247454/1911.

isation. The patent of Senderens [1] for the reduction of the vapours of nitrobenzene to aniline by hydrogen in presence of finely divided nickel is the first patent significant of the technical development which such catalytic hydrogenation would rapidly attain.

Application of the principle to liquid media was disclosed in the patent of Leprince and Sieveke [2] and in the corresponding British patent of Normann.[3] For this latter, which has been exploited in England by Messrs. Crosfield of Warrington, a fundamental character was claimed. It was decided (1913) in the English courts that the Normann patent could not be regarded as constituting a monopoly of processes for the hydrogenation of oils, and consequently many other patented processes are now being used for the purpose on a technical scale. The operation of the catalytic action in liquid medium has alone rendered this technical application possible, since only a small percentage of fats and oils can be vaporised without decomposition, rendering inapplicable, therefore, the well-known procedure of Sabatier and Senderens in the vapour phase.

The numerous processes proposed may broadly be classified under four distinct headings :

(1) Processes employing reduced nickel or other base metals.
(2) Processes employing the precious metals: platinum and palladium.
(3) Processes employing oxide of nickel and oxide catalysts in general.
(4) Processes employing organic salts of nickel.

Processes employing reduced nickel or other base metals.—These processes are applications to liquid media of the Sabatier-Senderens hydrogenation reaction. Nickel is known to be the best catalytic agent of the series, copper, iron, cobalt, and other metals having also been studied.

The preparation of the catalyst material is the most important matter in the attainment of efficient hydrogenation, the aim of the operation being the preparation of the metal in a finely divided condition. The researches of Sabatier and Senderens have shown, as previously emphasised, that the temperature of reduction of the oxide by hydrogen determines largely the properties of the catalyst. The oxide should be prepared from salts free from chlorine and sulphur, which act as poisons in the case of nickel. Copper is less sensitive to poisons, but also less active catalytically. The access of air or oxygen to the catalytic material should also be prevented, as oxidation readily occurs, even if the preparation be not pyrophoric..

The catalyst may be employed without any supporting material, intimacy of contact and uniformity being secured by agitating the oil.

[1] F.P. 312615/1901. [2] D.R.P. 141029/1902. [3] B.P. 1515/1903.

A process by Kayser has been patented on this principle.[1] The early patent of Normann indicates the possibility of rendering the catalyst more active by fixing it upon a porous support such as pumice. The use of other supports has also been proposed, as, for example, wood charcoal, metals, talc, kieselguhr, and infusorial earths generally.

The reduction may be carried out on the oxide either in the dry state or, alternatively, suspended in a portion of the oil to be hydrogenated. The former is the familiar laboratory process modified to technical conditions. While the catalyst produced may not be so active, it is more rugged than that reduced in oil. This latter method gives a catalyst which is very finely divided and of high activity. The colloidal nickel so produced, however, occasionally shows a tendency to agglomerate and to settle out of the oil mixture. The temperature of reduction of the oxide is sufficiently high that danger of altering the molecular condition of the oil by polymerisation—with consequent changes in taste—is possible and may adversely affect the hydrogenation product, if required for edible purposes. Dewar and Liebmann [2] showed that it was possible to lower the reduction temperature of nickel oxide by admixing with the oxide 10 per cent of cupric oxide. The lower reduction temperature thus secured would favour the production of a more active nickel. Armstrong and Hilditch [3] have shown that the copper-nickel oxide mixture must be achieved under certain prescribed conditions for the beneficial action on the temperature of reduction to be obtained. They ascribe the lowering of the reduction temperature to the effect of local overheating produced by the exothermicity of the reduction process in the case of copper oxide. Kahlenberg and Ritter [4] found that a 50 : 50 nickel-cobalt catalyst was superior to their nickel catalyst similarly prepared.

The temperature at which hydrogenation is carried out is governed by the nature of the compound to be treated and the catalytic agent used. For each compound there is a well-defined range of temperature for efficient operation. With nickel, for a number of oils, the range is from 160° to 200° with a temperature of maximum saturation velocity in the neighbourhood of 180°. With copper, the temperature is 200° and upwards.

Hydrogenation with base metal catalysts is carried out technically both at atmospheric pressure and under pressures of several atmospheres, the actual procedure adopted varying with the process employed. In certain processes the hydrogen under pressure is utilised to assist in spraying the oil in the hydrogenation chambers. In all cases the employment of pressures above the atmospheric will assist the progress of the catalytic action. The figures of Shaw [5] on the hydrogenation of oleic acid for the same period of time under varying pressures demon-

[1] U.S.P. 1004035/1911.
[2] B.P. 12981/1913 and 15668/1914.
[3] *Proc. Roy. Soc.*, 1922, **102A**, 27.
[4] *J. Physical Chem.*, 1921, **25**, 89.
[5] *Seifen. Zeit.*, 1912, **39**, 713.

strate the effect of pressure in diminishing the iodine value, and therefore also in raising the melting point of the material:

Pressures in Atmospheres.	Temperature.	Iodine No.
5	250°	77
25	250	64
50	250	52

Processes employing the precious metals.—The metals platinum and palladium, owing to their well-known catalytic activity, have received considerable study as agents for hydrogenation, and latterly their employment upon a technical scale, in spite of their rareness and consequent initial cost, has been successfully achieved.

The prevailing advantage in the use of rare metal catalysts would seem to lie apparently in the lower temperature of hydrogenation required. Thus, as early as 1906, Fokin had shown that, using palladium as palladium black, oleic acid could be reduced completely to stearic acid at a temperature of 80°-90°, whereas with reduced nickel a temperature 100° higher would be required in practice. With platinum in the form of platinum black the degree of reduction was not so great, only 24 per cent of stearic acid being formed.

The theoretical investigations of Paal and his co-workers,[1] of Willstätter,[2] and others have demonstrated conclusively that numerous hydrogenations can be effected in presence of finely divided platinum or of colloidal palladium as catalyst. In general it was found necessary to stabilise the colloidal metal, and various protective colloids were employed to effect this. Paal made use of a water-soluble protective colloid, the sodium salts of protalbinic or lysalbinic acids. Skita, who in his book *Über katalytische Reduktionen organischer Verbindungen*[3] has detailed in a comprehensive manner the literature of the subject, employed an acid-stable protective colloid such as gum arabic in place of the agents used by Paal. Solutions of platinum or palladium chloride in presence of such protective agents are reduced to stable colloidal solutions of the metal by means of hydrogen in the cold. The protective colloid also has the power of preventing the precipitation of the hydroxide of the metal when sodium carbonate is added to the solutions, the metal remaining in colloidal suspension. Such colloidal suspensions have proved to be excellent hydrogen carriers for hydrogenation of both aromatic and aliphatic unsaturated compounds. For technical operation, however, such stabilised colloidal catalytic agencies have little value, and the solution of the problem of technical hydrogenation by catalysts of the precious metal type was sought in another direction.

[1] *Ber.*, 1905–1909, **38, 40, 41, 42.** [2] *Ibid.*, 1908, **41**, 2199.
[3] F. Enke, Stuttgart, 1912.

Paal and the Vereinigte Chemische Werke of Charlottenburg have obtained numerous patents claiming the use of the noble metals for technical hydrogenation. The salts of the metals are employed in a powdered state, mixed with the fats to be hydrogenated, and treated with hydrogen at a pressure of several atmospheres at temperatures preferably below 100°.

The salts employed may be the simple compounds, $PdCl_2$, $PtCl_2$, $PtCl_4$, or the chloroplatinates, such as H_2PtCl_6, K_2PtCl_6, or the copper salt. Other acid radicals, *e.g.* the oxalate, may be substituted for chloride. They may be brought into the reaction medium either in the powdered state or in aqueous solution; or they may be added to the mass in a suspension in oil obtained by trituration of the solid with a small quantity of the oil to be hardened. In general, to prevent the formation, during reduction, of free acid from the salts employed, a sufficient quantity of a neutralising agent, such as anhydrous sodium carbonate, is also added. The use of carriers and porous supports for the metals is also indicated. Precipitated oxides and carbonates, talc, and infusorial earths are suggested. Further, metallic powders such as magnesium or nickel may also be employed to the same end. It is important both in the employment of double salts of the platinum metals and of metallic supports that metals should be employed which do not act anti-catalytically in the process. Thus in this connection it is to be observed that lead acts very markedly as anti-catalyst. The researches of Karl[1] have shown that hydrogenation is very slight when lead, aluminium, iron, or zinc are used as metal supports. Oxides, hydroxides, and carbonates of the first three metals have a similar anti-catalytic effect.

The use of the metallic salts is much more effective from the hydrogenation point of view than the use of corresponding amounts of the rare metals in the form of the sponge or of the metal black, both the velocity and the degree of hydrogenation being markedly improved. The time required for reduction depends upon the amount of rare metal salt used and also upon the pressure of the hydrogen. In an example cited by Paal in a patent specification, using 1 part of palladium as salt with 50,000 parts of castor oil, at a hydrogen pressure of 2-3 atmospheres and at a temperature of 80°, the completion of the reduction process, as recognised by the gas pressure remaining constant for some considerable time, could be attained in from six to eight hours.

The recovery of the catalyst after use is an operation of importance when a catalyst of considerable costliness is employed. The methods employed consist in the main of the destruction of the colloidal nature of the catalyst and the consequent precipitation thereof. This is attained by the addition of an electrolyte such as hydrochloric acid or of aluminium chloride, which electrolytes produce an immediate flocculation. With such means it has been found possible to hydro-

[1] Inaugural Dissertation, Erlangen, 1911, *Ber.*, 1913, **46**, 3069.

genate 100 kilos. of oil, employing 1-2 grms. of palladium, recovering from the reaction more than 90 per cent of the catalyst.

The use of other metals of the platinum series has also been investigated. The Vereinigte Chemische Werke [1] specifies iridium, rhodium, ruthenium, and osmium as catalytic material. Lehmann [2] hydrogenated small quantities of olive oil, starting with osmium tetroxide as catalytic material, which on hydrogenation produces a colloidal solution having markedly high activity. It is obvious, however, that the capital cost of such materials will in all cases hinder their employment upon the large technical scale.

Processes employing oxide of nickel and oxide catalysts in general.—Bedford and Erdmann [3] have claimed that oxides of nickel act as efficient carriers of hydrogen to oils and fats and that they possess certain advantages in practical employment over metallic nickel. The oxide catalyst is claimed to be less sensitive to sulphur and chlorine as poisons and to permit the use of hydrogen containing larger concentrations of impurities, notably carbon monoxide. They claimed that while both the sequioxide and monoxide are effective as hydrogen carriers, a nickel suboxide is the most efficient. A considerable patent literature arose [4] with reference to these oxide catalysts for hydrogenation and a considerable amount of technical development was initiated for such processes. It is possible that this arose in an effort to avoid infringement of patents covering the use of the reduced metal as catalyst.

A considerable controversy has taken place as to the nature of and activity of the supposed suboxide of nickel. Meigen and Bartels [5] claimed that the actual hydrogen carrier in the process was really metallic nickel. Bedford and Erdmann denied this, stating that the oil in which reduction was carried out hinders complete reduction. The catalyst upon removal from the hardened oil and after being freed from oil by benzol extraction is a strongly magnetic black powder, having a nickel content between that of the metal and nickelous oxide. It is said not to form nickel carbonyl when treated with carbon monoxide under conditions in which it would be readily obtained from the metal. Sabatier and Espil [6] found a slight inflection in the reduction rate of the oxide at a point which would correspond to a difficultly reducible oxide of the formula Ni_4O. Sabatier and Espil, however, proved the formation of nickel carbonyl with the product obtained at this stage of reduction. Moore [7] indicates the existence of a suboxide of nickel. Erdmann attempted the preparation of Moore's product, showed it to have the properties of the reduced material of Bedford and Erdmann,

[1] F.P. 425729/1911. [2] *Seifen. Zeit.*, 1913, **40**, 418. [3] *J. pr. Chem.*, 1913, **87**, 425.
[4] Bedford, B.P. 29612/1910; Bedford, Erdmann, and Williams, D.R.P. 62366; D.R.P. 260009/1911; F.P. Add. 18122/1913; Boberg and Techno-Chemical Laboratories, Ltd., B.P. 4702/1912.
[5] *J. pr. Chem.*, 1914, **89**, 301. [6] *Compt. rend.*, 1914, **159**, 668.
[7] *Chem. News*, 1895, **71**, 82.

to show colloidal properties towards oil, and to be a good hydrogenation catalyst.

Armstrong and Hilditch [1] have made a thorough study of the reduction of nickel oxides of different types. They conclude that the superior activity of a partially reduced product over a completely reduced metal is due to its being a " supported " catalyst, of the same type though not of the same degree of activity as nickel upon a support such as kieselguhr. The reduction curves are related to the physical condition of the oxide rather than to the formation of any more or less definite suboxides. They showed by experiment that the activity of a partially reduced product is dominated by the condition of the surface layer of reduced nickel. With non-supported catalysts, maximum activity is reached when only a portion of the nickel oxide has been reduced to metal; with a supported catalyst, however, which is not appreciably reduced in bulk by the process of reduction, the catalytic activity, instead of declining again, is maintained constant until and when the whole of the nickel oxide present has been reduced. It is therefore certain that variations in the catalytic activity of these reduced products are to be ascribed to variations in the nature of and area of free nickel exposed, and do not require for their interpretation the assumption of the presence of any catalyst other than the metallic nickel.

That the oxide is quite unnecessary for the production of an active nickel catalyst has recently been established in two other different researches. Kahlenberg and Ritter [2] showed that nickel chloride reduced with hydrogen at 180°-250° C. is a good catalyst for hydrogenation of oils. Kelber [3] also showed that the characteristics of a nickel catalyst prepared by reduction of nickel cyanide with hydrogen were identical in every way with those prepared from an oxygenated starting material.

Processes employing organic salts of nickel.—To avoid difficulties due to the presence of chlorine or sulphur in the catalyst preparations the use of salts of nickel containing none of these poisons is to be recommended. The organic salts of nickel have therefore been employed to a considerable degree for such purpose. As examples, the use of the formate, acetate, and lactate, of nickel carbonyl and of various fatty acid and amido-salts of nickel, is indicated in the literature of the subject. The use of salts such as formate and acetate forms the basis of a series of patent claims by Wimmer and Higgins.[4] By employing the formate, for example, Higgins claims that the velocity of hydrogenation is accelerated by presence of the formic acid. This latter may be present to the extent of 1 or 2 per cent, and may even be introduced along with the hydrogen by passing the gas before entering the reaction chamber through a solution of the volatile acid.

[1] *Proc. Roy. Soc.*, 1921, 99A, 490. [2] *J. Physical Chem.*, 1921, 25, 89.
[3] *Ber.*, 1924, 57, 136, 142. [4] B.P. 18282/1912; F.P. 441097/1911 and 454501/1913.

Alternatively, Wimmer and Higgins have proposed the preparation of catalysts by the reduction of such salts in a suitable protecting medium, such as the oil to be hydrogenated. After a period of time the oily mass becomes black in colour, the mixture thus obtained being added to the main body of oil to be hydrogenated. The temperature of hydrogenation is apparently 180°-200°. The nature of the catalyst thus obtained is doubtful. Commenting on these preparations, Erdmann states that the organic salts do not act themselves as catalysts. Bedford and Erdmann [1] claim that at 210° the salt is broken down, yielding the suboxide, which is the catalytic agent as in their process, whereas, at the higher temperature of 250°, metallic nickel is obtained. Incidentally, small amounts of nickel soaps result from the reaction. In order to suppress the concentration of free fatty acids resulting from such catalytic hydrogenation, Wimmer recommends the addition of drying agents to the catalytic material and proposes ignited sodium and magnesium sulphates for such purpose.

In order to promote intimacy of contact between catalyst and oil fat the use of nickel soaps as catalytic agents has been suggested. De Kadt [2] cites a mixture of the nickel and iron or copper soaps of fatty acids having a higher melting point than that of the hardened fat. After the catalytic operation is completed the soap is separated by agglomeration of the particles in the quiescent liquid or by filtration of the hot oil, the soap being retained on the filter. The aim in this method of operation is clearly to promote mutual solubility of contact material and substrate in order the more effectively to carry the hydrogen to the unsaturated fat. In the use of such materials, however, Bedford and Erdmann claim that the oxide and suboxide are the active agents.

Nickel carbonyl, $Ni(CO)_4$, the volatile compound discovered by Ludwig Mond and used so extensively in the preparation of pure nickel, has likewise been suggested as starting-point for the preparation of the catalyst. The claims of Shukoff [3] and of Lessing [4] may be mentioned in this connection. Nickel carbonyl is readily miscible with oil, and on heating to 200° is decomposed, depositing metallic nickel in a finely divided and active form. Lessing proposes the simultaneous introduction of the hydrogen and carbonyl in order to cause the formation of the metallic catalyst in the immediate presence of the hydrogen. He suggests that the gases employed need not be of great purity and that large amounts (up to 25 per cent) of carbon monoxide are permissible. Thus a hydrogen containing from 5 to 10 per cent of carbon monoxide may be passed over reduced nickel and thence direct to the oil maintained at a temperature of 200°-240°, the unabsorbed gases being returned to the starting-point for renewed passage over nickel and into the reaction mass. The amount of nickel required is said to

[1] *Loc. cit.*
[2] *E.g.* B.P. 18310/1912.
[3] D.R.P. 241823/1910.
[4] B.P. 18998/1912.

e small, excellent results being yielded by 0·1 part of nickel per 100 arts of oil. Ellis has studied the use of nickel carbonyl and records milar results,[1] observing, however, that the greatest difficulty attending s use appears to be "the removal of finer portions of the nickel recipitate from the oil after hydrogenation—but this may be accomlished by the observance of due precaution in filtration". The atalyst may, he further observes, be repeatedly used, and its egeneration is, relatively, a simple matter.

Maxted [2] has studied quantitatively the inhibiting effect of carbon onoxide upon the hydrogenation of an unsaturated glyceride in resence of finely divided nickel as a catalyst. There is a very marked oisoning effect, especially pronounced at the lowest concentrations f carbon monoxide. Thus, 0·25 per cent carbon monoxide decreased he hourly absorption of hydrogen by a third, whereas an additional ·75 per cent of the poison effected a further reduction of one-third in he amount of hydrogen consumed.

Mechanism of hydrogenation of unsaturated liquids.—In the realm f solid-liquid interface reactions at metallic surfaces, the studies of rmstrong and Hilditch [3] on the rate of hydrogenation of unsaturated ompounds at the surface of a nickel catalyst are both comprehensive nd convincing. Several workers, such as Fokin,[4] Moore, Richter, and an Arsdel,[5] Ueno,[6] Ubblehode and Svanoe,[7] and Thomas,[8] have bserved an approximation to a unimolecular action in hydrogenation f liquid systems at a nickel surface. Employing as pure materials as ould possibly be obtained, and working under mechanical conditions vouring maximum contact of the gaseous, liquid, and solid comonents of the system, Armstrong and Hilditch found that unsaturated lycerides containing mixtures of olein and less saturated glycerides ave characteristic curves, more nearly a series of two straight lines han a combination of two unimolecular curves. The first (almost near) segment corresponded to the portion of the process in which nalysis of the product has shown that the main action is the transrmation of less saturated glycerides to olein, and the second portion ot so straight) covers the part of the action in which olein (with the o-oleins also formed in this action) is passing to stearin.

Later, Armstrong and Hilditch extended the study to suitable unturated organic individuals which could be obtained in a state of eater purity than the non-volatile glycerides. The linear character the absorption of hydrogen–time curves became very definite. It was so shown how the linear curves could be transformed into unimolecular rves (i.) by the presence of a substance which slowly combines with

[1] *Hydrogenation of Oils*, p. 97 (Constable, London).
[2] *Trans. Farad. Soc.*, 1918, **13**, 36.
[3] *Proc. Roy. Soc.*, 1919, **96A**, 137; 1920, **98A**, 27; 1921, **100A**, 240.
[4] *Zeitsch. angew. Chem.*, 1908, **22**, 1451, 1492.
[5] *J. Ind. Eng. Chem.*, 1917, **9**, 451.
[6] *J. Chem. Ind. Tokio*, 1918, **21**, 749.
[7] *Zeitsch. angew. Chem.*, 1919, **32**, 257, 276.
[8] *J. Soc. Chem. Ind.*, 1920, **39**, 120.

the catalyst to form a permanent compound (permanent catalyst poisoning) or (ii.) by the accumulation of gaseous impurities in the gas-space above the acting system (thereby altering the otherwise constant concentration of hydrogen above the liquid). A further possibility resulting from this latter effect is that such gaseous impurities may have been preferentially adsorbed by the nickel catalyst and thus exercised a retarding influence on the reaction more than proportionate to their actual concentration in the gas phase. The linear curves obtained by Armstrong and Hilditch in these studies undoubtedly indicate that the chosen experimental conditions gave a catalyst surface which was, initially and for a prolonged period of time, completely saturated with reactants. The deviations from linearity in the later stages of the reaction are also to be ascribed in part to competition of reaction products for the nickel surface, since it has been shown [1] that even saturated hydrocarbon systems, *e.g.* ethane, cyclohexane, are strongly adsorbed by catalytic metals.

Throughout the preceding work the operating pressure of hydrogen gas was maintained constant. In a subsequent contribution Armstrong and Hilditch [2] discussed the influence of variation in the hydrogen pressure. In this investigation the greater complexity of the bimolecular reaction at an interface reveals itself quite definitely.

(i.) *Normal.*—In the absence of substituent groups of the kind discussed below, (iii.), and in presence of sufficient nickel (in general, so long as at least 0·1 per cent of nickel is present), the ethylenic union is hydrogenated at a rate which is in almost exact proportion to the absolute pressure of the hydrogen.

(ii.) *Subnormal.*—At very low concentrations of catalyst (say 0·01 to 0·02 per cent of nickel reckoned on the organic compound) the increase in rate of hydrogenation becomes less than proportional to the increase in pressure. The compounds which absorb hydrogen most readily are in general more prone to show this subnormal effect when the catalyst concentration is diminished, and it is especially marked in the case of multi-ethylenic compounds such as derivatives of linoleic acid or linolenic acid or with citral.

(iii.) *Abnormal.*—If the unsaturated compound contains another group which has affinity towards nickel (but is not open to hydrogenation), it is found that increase in hydrogen pressure causes an increase in the rate of hydrogen adsorption in more than simple proportion to the altered concentration of hydrogen. This has been observed with unsaturated alcohols and unsaturated carboxylic acids. Unsaturated aldehydes or ketones, on the other hand, show normal or subnormal behaviour.

The results are broadly, then, that increase in concentration of

[1] Pease, *J. Amer. Chem. Soc.*, 1923, **45**, 1196; Dougherty and Taylor, *J. Physical Chem.*, 1923, **27**, 533.

[2] *Proc. Roy. Soc.*, 1921, **100A**, 240.

hydrogen causes a directly proportionate increase in the rate of hydrogenation providing there are no disturbing factors; and that the increase in rate of hydrogenation becomes abnormally large if other groups active towards nickel but not open to hydrogenation are present. In other words, the nature of the organic compound has a determining influence on the effect of hydrogen concentration.

By analogy with results of Rideal and Pease on the mechanism of hydrogenation of ethylene at gas-solid interfaces the proportionality between rate and pressure in the normal case is to be ascribed to the fact that the extent of association between nickel and organic compound is large as compared with that between nickel and hydrogen. The accessibility of the hydrogen to free nickel surface (which will be small) varies directly as the hydrogen pressure. In the subnormal cases it is apparent also that the low concentration of nickel means a still lower accessibility of hydrogen to free nickel surface, the reduction in catalyst quantity being less unfavourable to the more strongly associated reactant, the unsaturated body. In the case of abnormal variation with pressure, the abnormality apparently lies in the secondary association of nickel with the unsaturated body at the second group which is not subject to hydrogenation. If it be assumed that this is a position of stronger association with nickel than the unsaturated linkage which can be hydrogenated, it follows that the influence of increased hydrogen pressure will be greater than in the case where only one type of association between nickel and unsaturated body is possible. It will need careful and painstaking research to verify such a point of view quantitatively. The work of Langmuir and Hardy previously cited is a beginning in that direction. Progress, however, may come more rapidly by the study of mechanism in vapour phase reactions, where, as Pease has shown, it is possible more easily to follow the variation of interfacial concentration.

Hydrogenation of Unsaturated Compounds (*continued*)

The acetylene linkage.—This is extraordinarily readily hydrogenated in presence of metallic catalysts. With nickel, acetylene and hydrogen in the volume ratio of 1 : 2 react so intensely that, with gas and catalyst originally cold, sufficient heat is developed to raise the temperature of the nickel to 150°. The product is a mixture of unchanged acetylene, some ethylene and saturated hydrocarbons, together with some carbon as a decomposition product. Excess of hydrogen favours ethane production. With excess acetylene, complex hydrocarbons, aliphatic, aromatic, and hydroaromatic, may be recovered from the product. Ross Culbertson and Parsons[1] have studied in detail the hydrogenation of acetylene to give ethylene. Nickel was employed as catalyst. They showed that, initially, a hydrogen-acetylene mixture gave mainly

[1] *J. Ind. Eng. Chem.*, 1921, **13**, 775.

ethane. This they ascribe to hydrogen already adsorbed by the nickel. When such hydrogen is consumed a product containing 80 per cent ethylene is obtained, the best results being given when the hydrogen is in slight excess of theory. As the acetylene in the mixture is increased, the ethane produced decreases and the sum of the ethylene and acetylene increases. The authors showed that both ethylene and acetylene will undergo hydrogenation at a temperature as low as $-10°$ C. with an active nickel catalyst. Paal and his co-workers [1] found that combination of hydrogen and acetylene occurs when a mixture of these gases is shaken with colloidal solution of platinum or palladium in water. With equal volumes of reactants the product contained 80 per cent ethylene. Copper is less suitable than nickel as a catalyst [2] owing to the formation of cuprene, a complex liquid hydrocarbon.

The carbon-nitrogen linkages.—The triple linkage between carbon and nitrogen is readily hydrogenated with metallic nickel as catalyst. The nitriles yield the corresponding primary amine :

$$RC{:}N + 2H_2 \longrightarrow R.CH_2.NH_2.$$

Secondary reactions occur, however, in presence of such a catalyst, and so a percentage of the product is composed of secondary and tertiary amines with an accompanying formation of ammonia :

$$2R.CH_2.NH_2 \longrightarrow (R.CH_2)_2NH + NH_3,$$

$$R.CH_2.NH_2 + (R.CH_2)_2NH \rightleftarrows (R.CH_2)_3N + NH_3.$$

The quadruple linkage between carbon and nitrogen present in carbylamines R . N : C is hydrogenated at 160°-180° in presence of nickel. Secondary amines of the type R . NH . CH_3 are the main product associated with small amounts of other amines.

The isocyanates, R . N : CO, yield at 180°-190° a secondary amine and water :

$$R.N{:}CO + 3H_2 = H_2O + NH\begin{<}R\\CH_3\end{.}$$

The water formed reacts with a portion of the isocyanate, forming a disubstituted urea $(R.NH)_2CO$ and carbon dioxide. The derivative of urea is in its turn hydrogenated, yielding water and a primary and secondary amine :

$$(RHN.)_2CO + 3H_2 = H_2O + NH_2R + R.NH.CH_3.$$

The carbon-oxygen double linkage.—Hydrogenation of the carbonyl group, CO, yields in general the corresponding secondary alcohol grouping, CH . OH. Aldehydes therefore yield the corresponding primary alcohols, with some tendency to hydrocarbon formation.

[1] *Ber.*, 1915, **48**, 275, 1195, 1202. [2] *Compt. rend.*, 1900, **130**, 1559.

Thus at 90° from formaldehyde some methane results along with the methyl alcohol; benzaldehyde yields some benzene and toluene at 210°-235° in presence of nickel. Aliphatic ketones yield secondary alcohols with ease by catalytic reduction, and the absence of secondary reaction products is remarkable, quantitative yields being frequent. Aliphatic ketonic acids are reduced to the corresponding hydroxy-acid; subsequent elimination of water may give rise to the lactone. Thus, lævulinic acid, at 250°, with nickel, yields γ-hydroxyvaleric acid, which is immediately converted to valerolactone,

$$CH_3 . CO . CH_2 . CH_2 . COOH \longrightarrow CH_3 . CH . CH_2 . CH_2 . CO + H_2O.$$

Aromatic ketones do not yield the secondary alcohol, but, on the contrary, the corresponding hydrocarbon. The quinones are readily hydrogenated to the corresponding dihydroquinones.

The benzene nucleus.—As is well known, the reduction of the benzene ring to more saturated cyclic products is, comparatively, a difficult operation by ordinary organic processes. Thus, with hydriodic acid as reducing agent, benzene does not yield cyclohexane but the isomeric methylpentamethylene, boiling at 69°. With the higher hydrocarbons, a certain quantity of open-chain aliphatic hydrocarbons always results. Moreover, such a procedure is not applicable at all to many of the benzene derivatives, such as phenol or aniline. Sodium amalgam and hydriodic acid have been employed with success, however, with acidic benzene derivatives.

The use of metallic catalysts has provided a method capable of fairly general application to the hydrogenation of the benzene nucleus. According to Sabatier it is undoubtedly the most important of the operations that reduced nickel has rendered possible in synthetic organic chemistry. At temperatures in the neighbourhood of 180° the aromatic nucleus may readily be hydrogenated in presence of nickel without isomerisation of the products or production of secondary reactions, and with, therefore, practically quantitative yields.

Early experiments of Lunge and Akunoff [1] had demonstrated a partial hydrogenation of benzene to cyclohexane, in presence of platinum black, at the ordinary temperature, or, better, at 100°. Palladium sponge, on the other hand, yielded cyclohexene, C_6H_{10}. The composition of the products was deduced from the contraction in volume of the gases and is therefore uncertain. The catalytic activity of the metal also rapidly diminished. The work of Sabatier and Senderens demonstrated the efficiency of the reduced nickel catalyst.

Thus, at temperatures above 70° benzene was directly hydrogenated to cyclohexane. The velocity of reaction attained a maximum in the temperature interval 170°-190°, and in this range cyclohexane

[1] *Zeitsch. anorg. Chem.*, 1900, **24**, 191.

was produced practically quantitatively with a single passage over the catalyst, no side reactions occurring. At higher temperatures, more especially above 300°, some methane was produced and carbon was deposited in small amount on the nickel. The higher homologues could similarly be treated, yielding the corresponding homologues of cyclohexane. If, however, the substituent group were complex, as, for example, ethyl, propyl, butyl, etc., a certain quantity of a lower homologue of the saturated six-membered ring was simultaneously produced. Thus, for example, from ethyl benzene, in addition to ethyl cyclohexane, methane and methyl cyclohexane were produced, whilst from propyl benzene both methyl and ethyl cyclohexene resulted, in addition to the propyl cyclohexane. A high reaction temperature favours this dissociation of the molecule into simpler components, so that, in general, a temperature not higher than 180° is employed.

An attempt was made by Dougherty and Taylor [1] to gain some insight, by kinetic measurements, into the mechanism of the catalytic reduction of benzene to hexahydrobenzene. The results indicated that the reaction does not occur at all according to the stoichiometric equation, as calculated from gas concentrations, but at rates governed by the distribution of the reacting materials between the catalyst and the gas phase. The trend of the reaction with change of temperature was studied. It was found that, above 230° C., quantitative yields could no longer be obtained. This has also been found by Pease and Purdum [2] with copper catalysts. These can be made reactive in the synthesis, contrary to the statements of Sabatier as to the absence of catalysis with copper. The deviations from complete reaction above 230° with nickel suggests that the catalysed reaction may be the formation of dihydrobenzene, which is then further saturated in the gas phase. Water vapour in small amounts, up to 2 per cent of the hydrogen volume used in the reaction mixture, had only a slight depressing effect on the reaction velocity. Carbon monoxide in small amounts, about 2 per cent of the hydrogen volume, had a very marked poisoning effect, particularly at low temperatures of 100° or under. As the reaction temperature was raised the poisoning was less noticeable. In large quantities, however, around 50 per cent of carbon monoxide, the reaction was completely stopped at 180°. Hexahydrobenzene, at low temperature, 100° or less, had a depressing effect on the reaction velocity. This effect disappeared at higher temperatures, in the neighbourhood of 180°. From experiments at 80° and 90° C. it was shown that the temperature coefficient of the reaction measured is approximately 3·1 : 1·9 or 1·65 per 10-degree rise. This is evidently the temperature coefficient of a chemical reaction as opposed to that of a diffusion process. Pease and Purdum show that benzene depresses the reaction velocity on copper catalysts.

The reversibility of the hydrogenation processes dealt with in these

[1] *J. Physical Chem.*, 1923, **27**, 533. [2] *J. Amer. Chem. Soc.*, 1925, **47**, 1435.

pages is most apparent in connection with the hydrogenation of the aromatic nucleus. Elevation of temperature favours the reverse reaction, so that, as the temperature is raised, the yield of hydrocarbons of the cyclohexane series diminishes. At temperatures above 230° the hydrogenation of the unsaturated bodies practically ceases, the reverse reaction completely prodominating. Elsewhere in this book the dehydrogenation processes receive a general treatment, so that further comment is not necessary in this place beyond the statement that a study of the equilibria in such systems offers a profitable field of investigation for the physical chemist interested in the application of physico-chemical measurement to synthetic organic processes.

Substituted benzenes with unsaturated linkages in the side chains are, naturally, converted by catalytic hydrogenation into the corresponding fully saturated hydrocarbons of the cyclohexane series. Thus, phenyl acetylene, $C_6H_5 . C \vdots CH$, yields practically exclusively ethyl cyclohexane.

Hydrocarbons containing several aromatic nuclei are transformed into the corresponding fully saturated compounds. Thus, diphenyl methane, $CH_2(C_6H_5)_2$, yields dicyclohexyl methane, $CH_2(C_6H_{11})_2$. Diphenyl, $C_6H_5 . C_6H_5$, yielded to Eykman [1] the compound $C_6H_5 . C_6H_{11}$, phenyl cyclohexane. Sabatier and Murat [2] obtained the saturated product, $C_6H_{11} . C_6H_{11}$.

Catalytic hydrogenation of the phenols, using nickel, occurs readily in the temperature interval 180°-220°. The corresponding hydroxy-derivatives of the cyclohexanes are obtained. Thus, phenol yields cyclohexanol with small quantities of cyclohexanone. The operation is, however, more difficult with polyphenols, since the temperature limits in which the reaction can be effected are narrow. If the temperature is too low, reaction velocity is small, whilst at more elevated temperatures decomposition of the molecule occurs with production of phenol and benzene, which then hydrogenate normally. Derivatives of phenol such as anisol, $C_6H_5O . CH_3$, may be hydrogenated below 150°.

Aromatic alcohols are not susceptible to catalytic hydrogenation without rupture of the molecule. Thus, benzyl alcohol yields toluene and methyl cyclohexane in presence of nickel at 150°.

Aromatic amines, as, for example, aniline, $C_6H_5 . NH_2$, yield the cyclohexyl amine with simultaneous formation of some ammonia, benzene, and cyclohexane, in addition to the formation of some derivatives of the secondary amine, $(C_6H_{11})_2NH$. Secondary alkyl aryl amines are readily hydrogenated in the aromatic nucleus at 160°-180°; thus methyl aniline yields methyl cyclohexylamine.

With aromatic acids the catalytic activity of the nickel ceases after a very brief interval, as was shown by Sabatier and Murat.[3] By hydrogenation of the esters, however, with subsequent saponification, these authors obtained an 80 per cent yield of the hexahydro-acid.

[1] *Chem. Weekblad*, 1903, **1**, 7. [2] *Compt. rend.*, 1912, **154**, 1390. [3] *Ibid.*, 923.

Miscellaneous ring structures.—The hydrogenation of ring structures, other than the aromatic ring, follows the same general principles as are outlined above for the benzene derivatives. The stability of the saturated ring, however, determines whether the end product is ring or open chain. Thus, cyclopropane yields propane. Cyclobutene gives first cyclobutane and then by further hydrogenation yields butane. Cyclopentadiene yields cyclopentane. Cyclohexene and cyclohexadiene both yield cyclohexane.

Tetravalent terpenes fix two molecules of hydrogen. The divalent terpenes fix one molecule. Thus, limonene, menthene, and cymene all yield menthane.

Naphthalene yields tetrahydronaphthalene with nickel at 200°. At 175° the hydrogenation may proceed further to decahydronaphthalene or naphthane. Similarly, the naphthols yield the corresponding decahydronaphthols. With anthracene, likewise, the hydrogenation is the more complete the lower the temperature at which the reaction is conducted.

Considerable technical development has occurred recently in the hydrogenation of naphthalene, the products tetrahydronaphthalene, decahydronaphthalene, and a mixture of the two, marked as "Tetralin Extra", have become familiar in the last few years. A factory of the Tetralin G.m.b.H. at Rodleben, near Breslau, has a plant with a daily capacity of 120 tons of the tetra-derivative. The technical problem is largely one of purification, the removal of thio-bodies from the material. This is attempted by a process of adsorption from the fused naphthalene by such agents as fuller's earth and kieselguhr, together with an alkali metal or even with spent nickel catalyst. The hydrogenation process is carried out in fused naphthalene at a temperature of 180°-200° C. under a working pressure of 15 atmospheres of hydrogen, a supported nickel catalyst being used. The hydrogenated products have found use as a turpentine substitute and as solvents.[1] The tetrahydro-derivative appears to be a promising material as starting-point for a new series of dyes. A very complete study of the hydrogenated naphthalenes has been given by Schroeter.[2] Braun and Kirschbaum [3] have extended Schroeter's studies to the hydrogenation of indene and acenaphthene in the pure liquids with nickel catalysts.

Heterocyclic compounds may be reduced in presence of nickel. Pyrrol gives a 25 per cent yield of pyrrolidine. Pyridine is only slowly reduced, but yields open-chain compounds and not piperidine. Quinoline gives an excellent yield of tetrahydroquinoline.

Hydrogenation with Rupture of the Molecule

As exemplified in several instances cited in the previous sections, hydrogenation in presence of metallic catalysts results in a rupture of

[1] Vollmann, *Farben-Zeit.*, 1919, **24**, 1689. [2] *Annalen*, 1922, **426**, 1. [3] *Ber.*, 1922, **45**, 1680.

the molecule in addition to hydrogenation of the molecule and of the products of the rupture. Thus there is a general tendency for long-chain hydrocarbons to break down into simpler molecules during the hydrogenation process. Similar behaviour was noted with the substituted benzene hydrocarbons. The production of hydrocarbons other than ethane in the hydrogenation of acetylene is to be attributed to the same cause, the setting at liberty of the two CH radicals leading to combinations of various forms. Sabatier and Senderens, by treating acetylene with hydrogen in presence of nickel, obtained as much as 20 c.c. of a clear yellow liquid quite comparable with natural petroleum, possessed even of a slight phosphorescence as is usual with the natural product, and in which higher saturated hydrocarbons, such as pentane, hexane, heptane, octane, nonane, decane, etc., were all present. By suitable modifications of the *modus operandi*, yields of liquid could be obtained with properties corresponding in different samples with the various petroleums from different oil-bearing districts. The different types of oils were produced with such success that Sabatier suggested the theory that many such natural oils had been formed in such manner by catalytic action of metals on mixtures of gases in the earth's interior. This work forms an important contribution to the subject of the origin of petroleum oils.[1]

The anhydrides of fatty monobasic acids rupture when hydrogenated at 180° and yield an acid and an aldehyde:

$$(R.CO)_2O + H_2 \longrightarrow R.COOH + R.CHO.$$

The latter is, naturally, partially reduced to the corresponding alcohol in the process.

Hydrogenation of ethers is difficult catalytically, but when conducted above 250° rupture occurs, yielding the hydrocarbon and alcohol corresponding, the latter itself being further ruptured in part, *e.g.*

$$(C_2H_5)_2O + H_2 \longrightarrow C_2H_6 + CH_3.CH_2.OH,$$
$$CH_3.CH_2.OH = CH_3.CHO + H_2 = CH_4 + CO + H_2.$$

The action in the case of alkoxy-derivatives of benzene has already been cited. Below 150° they hydrogenate normally in the nucleus. A certain amount of rupture simultaneously occurs, yielding cyclohexane and the aliphatic alcohol. Above 300°, however, no hydrogenation of the nucleus occurs, and the products are phenol and the aliphatic hydrocarbon or benzene and the aliphatic alcohol:

$$C_6H_5.OR + H_2 \longrightarrow C_6H_5.OH + RH,$$
$$C_6H_5OR + H_2 \longrightarrow C_6H_6 + ROH.$$

Numerous examples of rupture of nitrogen-containing compounds have already been cited.

[1] Sabatier and Senderens, *Compt. rend.*, 1899, **128**, 1173; 1900, **131**, 187, 267; 1902, **134**, 1185.

Selective hydrogenation.—The term selective hydrogenation may be used to indicate the preferential saturation of one or more double bonds in compounds containing several unsaturated centres. Several examples of such selectivity have already been discussed. Thus, unsaturated ketones may be catalytically converted to the saturated ketone without simultaneous reduction of the ketonic grouping. Unsaturation in a side chain may be removed without hydrogenation of the benzene nucleus. The problem acquires both theoretical and technical significance when reference is made to the selective hydrogenation of ethylenic bonds in long hydrocarbon chains. In the hydrogenation of oils the possibility exists of the conversion of the less saturated glycerides of linoleic and linolenic acids into glycerides of oleic acid before the latter are transformed into stearin.

Paal and his co-workers,[1] in their studies of catalytic hydrogenation in presence of the colloidal platinum metals, showed that such a stepwise reduction could be achieved in this manner when the two double bonds in the compound were separated by more than two carbon atoms. They showed, on the other hand, that, with a system of conjugated linkages—C : C . C : C—no selective hydrogenation occurred, the completely saturated product being produced.

H. K. Moore, Richter, and van Arsdel,[2] from a study of the rate of hydrogenation of cotton-seed oil, concluded that the process was selective, linolein passing to olein before any appreciable amount of olein was hydrogenated. Hilditch and C. W. Moore[3] showed, by analysis of samples withdrawn at intervals from the hydrogenation system, that, in a wide variety of oils (cotton-seed oil, ethyl esters of cotton-seed oil acids, maize, soya bean, and linseed oils), hydrogenated at 180° C. with nickel and, in some cases, with copper catalysts, the amount of saturated derivatives present does not sensibly increase until the amount of linoleic derivatives has fallen to 10 per cent or less of the mixture. Correspondingly, the percentage of oleic derivatives increases at the expense of the linoleic compounds up to the same point. The free fatty acids from cotton-seed oil constituted an exception in which the hydrogenation was only partially selective. Richardson, Knuth, and Milligan[4] have recently confirmed this conclusion with cotton-seed oil in presence of nickel, using a new method of analysis of the various products. They find the selectivity of the hydrogenation process to be more marked with increasing amounts of catalyst and with increasing temperatures up to an optimum in the neighbourhood of 200° C. More recently[5] the same authors have shown that with marine oils, such as menhaden or whale oil, the more highly unsaturated glycerides are hydrogenated without formation of substantial quantities of completely saturated bodies. An abrupt change occurs at an iodine

[1] *Ber.*, 1912, **45**, 2221.
[2] *J. Ind. Eng. Chem.*, 1917, **9**, 451.
[3] *J. Soc. Chem. Ind.*, 1923, **42**, 15T.
[4] *J. Ind. Eng. Chem.*, 1924, **16**, 519.
[5] *J. Ind. Eng. Chem.*, 1925, **17**, 80.

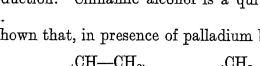
value of approximately 84, at which nearly all the esters of more than two double bonds have disappeared. Below this critical point, hydrogenation results both in the formation of saturated acids and in the conversion of C_{20} and C_{22} acids containing two double bonds to corresponding acids of one double bond. Here, evidently, the principle of selectivity is only partial. One may venture as a possible explanation the view that the members non-selectively hydrogenated may have a conjugated double bond system, as indicated earlier in reference to the work of Paal.

The several facts disclosed by these researches indicate that the relative extents of adsorption of the more and less saturated compounds is one of the factors which determines the selectivity of the hydrogenation process. One would conclude from the results that the more highly saturated glycerides are preferentially adsorbed to a marked degree, especially in the lower temperature interval. As the temperature rises beyond 200° C. this preferential adsorption becomes less pronounced. Furthermore, preferential adsorption should, from these results, be less marked in the case of the acids than in the case of the glycerides. While quantitative data on selective adsorption in liquid systems of this kind are almost entirely lacking, the conclusions cited are to be anticipated from adsorption studies in solid-gas systems. There is a fruitful field for investigation here, preferably with simpler unsaturated systems than are the natural oils.

Rideal [1] has studied the relative rates of hydrogenation of the sodium salts of cinnamic and phenyl propiolic acids in presence of palladium sol protected by gum arabic. He found that, at low sol concentrations, the phenyl propiolate is hydrogenated at approximately twice the rate of the cinnamate under the same experimental conditions. This suggests that the salt is not desorbed from the sol surface until completely saturated and that the propiolate takes up two hydrogen molecules in the same time as the cinnamate takes up one.

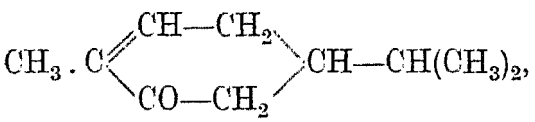
Armstrong and Hilditch have recently indicated [2] the variability of the selective nature of the process with different organic molecules. Cinnamic aldehyde is first hydrogenated to phenyl propionic aldehyde. This latter is reduced, but not as rapidly as it is formed. Phenyl propyl alcohol and the corresponding ether are the main products of the secondary reduction. Cinnamic alcohol is a quite minor product of hydrogenation.

Vavon [3] has shown that, in presence of palladium black, carvone

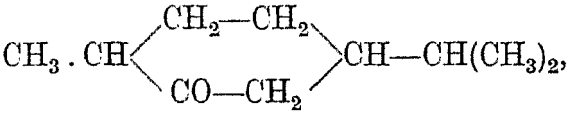


[1] *Trans. Farad. Soc.*, 1923, **19**, 90. [2] *Chemie et Ind.*, August 12, 1924.
[3] *Compt. rend.*, 1911, **153**, 68.

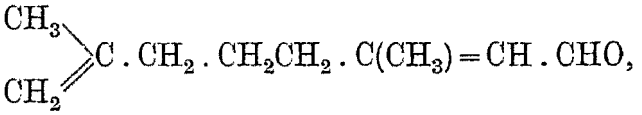
transformed by hydrogen into carvotanacetone



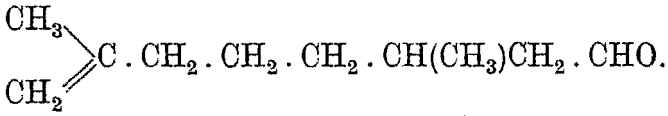
ien into tetrahydro-carvone



nd finally into the corresponding secondary alcohol. Armstrong and ilditch observed the same reaction with nickel. They also have own that citral,



ves, first of all, citronellal,



bsequent hydrogenation is characterised by a predominance of the duction of the aldehyde group with formation of citronellol, which omerises for the most part into isopulegol, which is then hydrogenated menthol.

The hydrogenation of carvone differs then from that of citral in at, in the one case, the ethylenic linkage adjacent to the carbonyl oup is the first to be attacked, whilst in the other case the opposite true. In addition, the carbonyl group is the last to be attacked in rvone; in the case of citral it disappears before the second ethylenic nd is hydrogenated. Here are interesting problems in oriented sorption, or in bond stability.

Vavon and his students have multiplied such cases of selective drogenation. They have studied the distribution of hydrogen be- een two unsaturated bodies and between unsaturated groups in the me compound.[1] The method of experimentation has in each case en the study of the rate of hydrogenation in liquid system or in lution, using colloidal platinum as catalyst. Recently, Vavon has mmarised his researches [2] with a view to showing that the phenomenon steric hindrance, familiar in esterification, addition of bromine to ganic molecules, and the reactivity of oximes, is also operative catalytic hydrogenation. Thus, in the distribution of hydrogen

[1] See, for example, Vavon and Kleiner, *Compt. rend.*, 1923, **176**, 401; Vavon and Husson, *mpt. rend.*, 1923, **176**, 989; Vavon and Ivanoff, *Compt. rend.*, 1923, **177**, 453; Vavon, *mpt. rend.*, 1910, **150**, 1127; 1911, **152**, 1675; 1911, **153**, 68.

[2] *Rev. Gen. Sci.*, 1924, **35**, 505.

between an ethylenic hydrocarbon, C_7H_{14}, on the one hand, and either pinene or undecylenic acid on the other, the unsaturated hydrocarbon, C_7H_{14}, is progressively less hydrogenated as we proceed from ethyl propyl ethylene, the straight chain body, to trimethyl ethyl ethylene. Similar results are obtained with cinnamic acid, the α- and β-methyl, and the α-dimethyl cinnamic acids.

CHAPTER IX

DEHYDROGENATION

CATALYTIC methods of eliminating hydrogen from organic compounds have become important in two branches of industrial chemistry, viz. the preparation of aldehydes from alcohols according to the equations

$$C_nH_{2n+1}.CH_2.OH \rightleftarrows C_nH_{2n+1}CHO + H_2,$$
$$C_6H_5.C_nH_{2n}.CH_2.OH \rightleftarrows C_6H_5.C_nH_{2n}.CHO + H_2,$$

and the cracking of hydrocarbons into fractions of lower boiling point, *e.g.* paraffins into petrols, ligroin, benzene, and other aromatic polycyclic hydrocarbons.

Processes of catalytic hydrogenation are usually reversible ; indeed, this is so in all cases where the products remain in the same phase during hydrogenation or dehydrogenation.

Thus, benzene can be converted into cyclohexane by hydrogenation over reduced nickel at 70°-200°. At 270°-280° cyclohexane undergoes dehydrogenation to benzene in presence of the same catalyst.

We may thus consider the reaction

$$C_6H_6 + 3H_2 \rightleftarrows C_6H_{12}$$

as strictly reversible.

In this and in many other cases the process of hydrogenation proceeds most rapidly at low temperatures, the equilibrium amount of the unsaturated compound being negligible at the usual temperatures of operation.

With elevation of the temperature all the components of the system are usually present in sufficiently large amounts to be capable of measurement, and it is practically certain that in the hydrogenation of benzene below 270° the equilibrium constant

$$K = \frac{[C_6H_6][H_2]^3}{[C_6H_{12}]}$$

could be arrived at from either side.

Dougherty and Taylor[1] attempted to evaluate this equilibrium

[1] *J. Physical Chem.*, 1923, **27**, 533.

constant at various temperatures with nickel catalysts but obtained no satisfactory data. Zelinski and Pawlow[1] used platinised asbestos and palladium. They showed that dehydrogenation of cyclohexane was already marked at 150° C. and that the action becomes rapidly more marked as the temperature rises. Platinum and palladium are superior to nickel for the purposes of an equilibrium study, since the authors note that no deposition of carbon occurs even at 408° C. Zelinski showed that the dehydration was selective, in that other saturated cyclic hydrocarbons could not be dehydrogenated. Thus, in a mixture of cyclohexane and cyclopentane only the former underwent the dehydrogenation process, which could therefore be used as a method of separating such bodies. Zelinski has applied such processes of dehydrogenation to a study of the constituents of the naphthenes in naturally occurring petroleums, and has shown that natural naphthenes of petroleum are mainly cyclical but are not hexahydroaromatic compounds.[2] Cyclohexane always yields a varying amount of methane when undergoing catalytic dehydrogenation :

$$3C_6H_{12} \longrightarrow 2C_6H_6 + 6CH_4,$$

whilst methane resulting from the hydrogenation of carbon monoxide at 180°-200° in the presence of reduced nickel commences to undergo dehydrogenation with the deposition of carbon at 350°-390° :

$$CH_4 \longrightarrow C + 2H_2.$$

Owing to the low vapour pressure of carbon at these temperatures, rehydrogenation of the deposited carbon does not proceed on lowering the temperature to 200°, and practically complete removal of the methane may be effected.

The reversibility of the hydrogenation process, even in the case of fatty oils, is indicated by a patent to Levey,[3] who claims dehydrogenation of such bodies by subjecting them to the action of a catalytic agent in the vapour phase at temperatures exceeding those under which hydrogenation is accomplished. Normann[4] has confirmed this behaviour, which occurs even in the presence of hydrogen, although better results are obtained by using a current of another gas, preferably carbon monoxide. Normann suggests that these results afford a possible explanation of the difficulty of reducing the iodine number of an oil to zero by catalytic hydrogenation and of the appearance of new unsaturated acids in the oil-hardening process, owing to the addition of hydrogen atoms in one part of the molecule and the splitting-off of others elsewhere.[5] Brochet records anomalous results with castor oil,[6] which indicate that the same phenomenon may occur with this oil.

[1] *Ber.*, 1923, **56**, 1249. See also Zelinski, *Ber.*, 1911, **44**, 3121 ; 1912, **45**, 3677.
[2] *Ber.*, 1923, **56**, 787, 1716, 1718, 1723.
[3] U.S.P. 1374589.
[4] *Chem. Umschau*, 1923, **30**, 3 ; *J. Soc. Chem. Ind.*, 1923, **42**, 149A.
[5] See C. W. Moore, *J. Soc. Chem. Ind.*, 1919, **38**, 320r ; Hilditch and C. W. Moore, *J. Soc. Chem. Ind.*, 1923, **42**, 15r.
[6] *Bull. Soc. Chim.*, 1923, **33**, 626.

The Preparation of Aldehydes from Alcohols

We have already noted that, in the preparation of formaldehyde from methyl alcohol, the initial stage of the reaction is a process of dehydrogenation :

$$CH_3 . OH \rightleftarrows H . CHO + H_2,$$

but, owing to the fact that all catalysts hitherto employed to bring about this reaction gradually lose their activity, for some cause with no satisfactory explanation as yet, the preparation of formaldehyde has been transformed into a fractional combustion process. The higher alcohols of the aliphatic series, as well as aromatic alcohols, can likewise undergo conversion into aldehydes with elimination of hydrogen in the presence of catalysts, and as such catalytic materials do not appear to lose their activity appreciably even with prolonged running, the technical development of such processes has been possible.

The dehydrogenation of primary alcohols is a reversible action :

$$R . CH_2 . OH \rightleftarrows R . CHO + H_2.$$

Hydrogenation of the aldehyde in the presence of reduced nickel proceeds rapidly at 180° in the case of the aliphatic compounds and below 230° for aromatic aldehydes.

Rideal[1] has shown that with ethyl and isopropyl alcohols the dehydrogenation equilibria can be fairly satisfactorily determined at low pressures of the gaseous system, and that the results obtained could be utilised to evaluate the thermal data for the reactions. Thus, for the dehydrogenation of ethyl alcohol a value of $\Delta H = 11{,}500$ cals. was obtained, in fair agreement with data from the heats of combustion of the organic substances.

At high temperatures, however, two other important side reactions proceed with measurable velocity, tending to lower the yield of aldehyde :

(*a*) The formation of saturated hydrocarbons by elimination of CO :

$$R . CHO \rightleftarrows RH + CO.$$

Below 300° only small amounts of hydrocarbon are obtained with the aliphatic aldehydes, but the loss due to this reaction is usually somewhat higher in the aromatic series.

(*b*) Dehydration of the alcohol with the formation of unsaturated hydrocarbons :

$$R . CH_2 . CH_2 . OH \rightleftarrows R . CH : CH_2 + H_2O,$$

a reaction which proceeds fairly rapidly at 400° in the presence of catalysts.

[1] *Proc. Roy. Soc.*, 1921, 99A, 153.

The employment of metallic catalysts in the preparation of aldehydes.—In the conversion of ethyl alcohol to acetaldehyde, metallic copper, obtained by reduction of fused copper oxide, gives the most satisfactory results. Formation of aldehyde can already be observed at 200°, but the optimum temperature for operation lies in the neighbourhood of 310° with a permissible latitude of some 20°. At 420° more than 16 per cent of the acetaldehyde is converted into hydrocarbons. With relatively low space velocities (*circa* 200) a 20 per cent conversion can be effected at normal temperatures of operation. The resulting mixture of aldehyde and alcohol vapour mixed with hydrogen and a very small quantity of aldehyde condensation products are passed to a relatively large copper fractionating column, whence the alcohol can be recovered and returned to the preheater situate in front of the catalyst tubes. The aldehyde and hydrogen recovered from the middle section and top of the dephlegmating column respectively are practically pure. It is said that the conversion of alcohol into aldehyde by this means is attended with a loss of well below 10 per cent when the due precautions are taken as regards temperature control.

Propyl, butyl, isobutyl, and isoamyl alcohol undergo similar processes of dehydrogenation with formation of the respective aldehydes at temperatures varying between 220° and 300° in the presence of metallic copper. Bouveault[1] cites the dehydrogenation of decyl alcohol, $C_{10}H_{21}$. OH, under reduced pressure by similar means.

The most thorough study of the dehydrogenation process at a copper surface with a series of the saturated alcohols has been made by Palmer and his associates.[2] The outstanding result of this work is that, on a given catalyst, the rates of dehydrogenation of the primary alcohols, ethyl, propyl, butyl, isobutyl, and isoamyl, are all equal within the limits of experimental error, and the temperature coefficient is the same for all. Secondary propyl alcohol reacts with a velocity about five times that of the primary alcohols and has a slightly higher temperature coefficient. The results, taken in conjunction with the probable assumption that the activated layer of molecules is unimolecular, show that these alcohols are adsorbed with the CH_2OH group in contact with the copper surface and the hydrocarbon chains perpendicular to the surface. Constable, in the last of the series of these researches, shows that the reaction velocity at 250° C. with ethyl and butyl alcohols was independent of the pressure in the range 10-140 cm. of mercury. It is evident therefore that, in this pressure range, the surface is practically covered with alcohol molecules and the mean life of the molecule in the activated unimolecular layer changes only slowly with the pressure over the range investigated.

The investigation of this reaction has been extended by Sabatier[3]

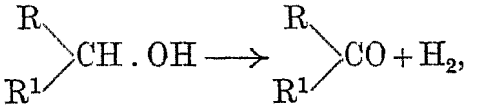
[1] *Bull. Soc. Chim.*, 1908, **4**, 3, 50, 119.

[2] *Proc. Roy. Soc.*, 1920, **98A**, 13; 1921, **99A**, 412; 1922, **101A**, 178; 1924, **106A**, 250; 1925, **107A**, 255, 270, 27.

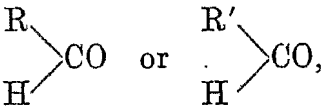
[3] *Ann. Chim. Phys.*, 1905, **8**, 4, 467.

nd by Bouveault [1] to secondary alcohols of the aliphatic series as well s to a certain number of aromatic aliphatic derivatives.

Owing to the fact that the ketones prepared by the dehydrogenation f the secondary alcohols, according to the general reaction



re more stable than the corresponding aldehydes,



emperatures higher than 300° can usually be adopted, resulting in a nore effective conversion of alcohol into ketone by one passage over he copper catalyst. Sabatier states that temperatures up to 400° an be employed with safety, and that a conversion of more than 75 per ent can be effected by this means.

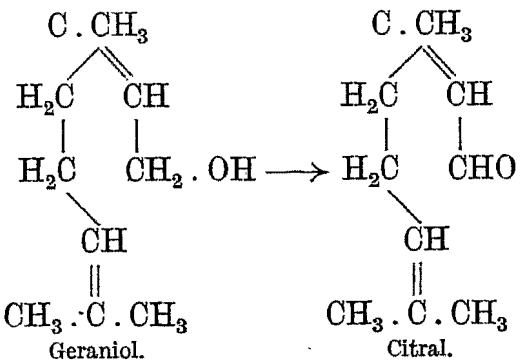
Dehydrogenation of isopropyl alcohol commences at 150°, whilst elow 300° the loss due to the formation of propylene is negligible. 2-Butyl and 2-octyl alcohol are comparatively easily dehydrogenated t 300°, whilst the formation of the unsaturated hydrocarbons does ot commence to be appreciable until 400°.

Aliphatic alcohols containing a double bond, *e.g.* allyl alcohol, $CH_2 : CH . CH_2 . OH$, are usually converted into the saturated ldehydes :

$$CH_2 : CH . CH_2 . OH \longrightarrow CH_3 . CH_2 . CHO,$$

simultaneous process of dehydrogenation and hydrogenation.

According to Bouveault [2] geraniol is an exception, since citral is ractically the only product produced by passage over reduced copper t 200° under reduced pressure :

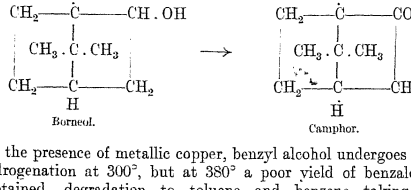


Geraniol. Citral.

The absence of cymene in the citral, which can be easily formed by the elimination of water and closure of the ring, is under these conditions of dehydrogenation somewhat unexpected. Borneol, likewise,

[1] *Bull. Soc. Chim.*, 1906, **3**, 35, 650. [2] *Loc. cit.*

can be converted practically quantitatively into camphor at 300° : [1]



In the presence of metallic copper, benzyl alcohol undergoes partial dehydrogenation at 300°, but at 380° a poor yield of benzaldehyde is obtained, degradation to toluene and benzene taking place simultaneously.

The conversion of phenyl ethyl alcohol, on the other hand, into the corresponding aldehyde is easily effected under reduced pressure.

Sabatier and Senderens [2] have investigated the dehydrogenation of the alcoholic derivatives of cyclohexane. With cyclohexanol itself, the cyclohexane produced at 300° undergoes but little secondary decomposition, but with the various methyl cyclohexanols by-products such as the unsaturated ring compounds and cresols increase in amount with elevation of the temperature.

Knoevenagel and Heckel [3] record an interesting case of ether formation with metallic copper at 280° :

$$C_6H_5 . CH . OH . C_6H_5 \longrightarrow \begin{matrix}(C_6H_5)_2CH\\(C_6H_5)_2CH\end{matrix}\!\!>O + H_2,$$

whilst the conversion into benzophenone :

$$C_6H_5 . CH . OH . C_6H_5 \longrightarrow \begin{matrix}C_6H_5\\C_6H_5\end{matrix}\!\!>CO + H_2,$$

occurs when heated in the absence of copper to 280°-295°. Sabatier cites this example as the only exception to the processes of dehydrogenation catalytically accelerated by the presence of reduced copper. It is interesting to note that these observers found that the preparation of benzophenone by this process of dehydrogenation could easily be effected in the presence of palladium black. Nickel is even more active than copper as a dehydrogenation catalyst. Thus, ethyl and the other aliphatic alcohols already undergo appreciable conversion some 50 degrees below that found necessary in the presence of copper. Degradation of the aldehyde or ketone produced is, however, as a rule, much more marked, thus limiting the utility of this metal. For

[1] Goldsmith, B.P..17573/1906.

[2] *Ann. Chim. Phys.*, 1905, **8**, 4, 467.

[3] *Ber.*, 1903, **36**, 2816.

xample, 75 per cent of the propyl aldehyde produced by the dehydro-enation of propyl alcohol at 260° is destroyed during its passage over he catalyst material.

Sabatier and Senderens[1] state that reduced cobalt is intermediary etween the last two elements in catalytic activity, whilst platinum nd palladium exert an activity similar to that of nickel, although econdary degradation does not proceed to such a great extent. Thus, n the dehydrogenation of ethyl alcohol in the presence of platinum lack, although conversion commences at 270° the rapidity of conver-ion is not marked until a temperature of 370° is reached, when a 5 per cent loss of acetaldehyde is obtained as a result of secondary egradations into methane and carbon :

$$C_2H_5 . OH \longrightarrow CH_3 . CHO + H_2,$$
$$CH_3 . CHO \longrightarrow CH_4 + CO.$$

Experiments with both zinc and brass have given unsatisfactory results, ccording to Ipatiew,[2] but brass has been used technically for the ehydrogenation of ethyl alcohol.

The use of metallic oxides.—In the preparation of formaldehyde rom methyl alcohol we have already noted that the use of certain xides, notably those of aluminium and manganese, as catalytic naterials has been attended with definite although somewhat poor ields of the aldehyde.

The extension of the use of certain oxides to the dehydrogenation f the higher alcohols has been made by Sabatier and Mailhe,[3] who rrived at the conclusion that they were less satisfactory than the netals owing to their lower reactivity, thus necessitating the use of igher temperatures with a resulting increase in the secondary forma-on of hydrocarbons and carbon monoxide. These investigators have assified the oxides investigated into three groups :

(*a*) Those in which the catalytic activity for processes of dehydro-enation is most marked, *e.g.*

$$R . CH_2 . OH \longrightarrow R . CHO + H_2.$$

hese include uranium, molybdenum, zinc, and vanadium oxides.

(*b*) Those in which processes of dehydration are accelerated, *e.g.*

$$R . CH_2 . CH_2 . OH \longrightarrow R . CH = CH_2 + H_2O,$$

ncluding non-calcined chromium oxide, silica, and titanium oxide.

(*c*) Those which accelerated both reactions ; including the oxide of ucinum, zirconia, and calcined chromium oxide.

With manganese oxide, dehydrogenation of the aliphatic alcohols oes not commence below 360°, at which temperature the conversion

[1] *Ann. Chim. Phys.*, 1905 (viii.), **4**, 473.
[2] Ipatiew, *Ber.*, 1901, **34**, 3579, and 1904, **37**, 2961.
[3] *Ann. Chim. Phys.*, 1910 (viii.), **20**, 313.

is only one-fortieth of that brought about by reduced copper under similar conditions, and secondary decomposition is already quite marked.

Both the oxides of cadmium and tin exhibit interesting phenomena, in that their reactivities at 300° are comparable to those of metals; simultaneous reduction to metal, however, occurs. The metals themselves exhibit marked catalytic activity above their melting points, but owing to the gradual growth of large drops of the liquid metal at the expense of the smaller ones on account of their smaller vapour pressure the active surface of the catalyst is slowly reduced, causing a corresponding reduction in the space time yield for a given size of converter.

The Cracking of Oils

The "cracking" or resolution of hydrocarbons of high boiling point of the aromatic, and more especially of the aliphatic, series into simpler hydrocarbons, both saturated and unsaturated, of relatively low boiling point, is now a well-established industry. In principle the most effective agencies for accomplishing these changes are temperature and pressure, but the influence of catalysts, apart from the specific action of surface contact, both on the velocity of conversion and also on the nature of the product obtained, is so marked that their industrial significance is now a matter of importance. At the same time, a study of their behaviour, although not throwing much light on the nature of the catalytic processes involved, is giving valuable information as to the methods of formation of the various products in the pyrogenetic decomposition.

To Murdock (1792) must be given the credit for the observation that the effect of heat on heavy oil was to produce a gas suitable for illumination. Since that time the cracking of heavy oils has been stimulated by the following factors: (i.) the relative increase in output of very heavy oils over paraffin, petrol, and natural gas owing to the increased rate of consumption of the latter; (ii.) the increased demand for petrols and petrol ethers as fuels for internal combustion engines and solvents; for paraffin in the stationary power engines of small sizes and for illumination, and for aromatic hydrocarbons as raw materials in the chemical industries.

The primary decomposition of an aliphatic hydrocarbon into its simpler constituents prior to the rearrangement by synthesis of these decomposition products into open- or closed-chain hydrocarbons is the explanation of the "cracking" process now generally adopted. All evidence [1] points to the hypothesis that catalysts exert a considerable activity in the decomposition of the original hydrocarbon and may

[1] See the carefully compiled literature by Lomax, Dunstan, and Thole, *J. Inst. Pet. Tech.*, 1916, **3**, 9, 36-120.

exert a marked influence in the secondary synthesis. Since, in general, degradation and synthesis in the reactions cannot be separated, the exact functions of the catalysts employed must be considered at present as merely speculative in character.

Two alternative theories have been advanced to interpret the mechanism of the first or disintegrating stage of the cracking process, that of Berthelot[1] and the more recent one of Bone and Coward.[2]

According to Berthelot disruption proceeds in stages with the primary elimination of hydrogen, with or without the simultaneous formation of methane and the production of an olefinic hydrocarbon containing one or more double bonds. Thus, ethane may be considered to undergo the following alternative or simultaneous pyrogenetic decompositions:

$$C_2H_6 \rightleftarrows H_2C:CH_2 + H_2,\quad 2H_2C:CH_2 \rightleftarrows C_2H_6 + HC\vdots CH$$

$$\downarrow\uparrow$$

$$HC\vdots CH + H_2$$

$$2C_2H_6 \rightleftarrows HC:CH + 2CH_4 + H_2$$

$$\uparrow\downarrow$$

$$C_2H_6 + H_2.$$

The intermediary formation of olefines as well as of di- and triolefines during the thermal decomposition of a paraffin is a well-known phenomenon, having been confirmed by the researches of Thorpe and Young,[3] Haber,[4] and others. It is, furthermore, a matter of great technical importance in the preparation of motor spirits, since, on storage, especially under the influence of light, the di- and triolefines polymerise to form a gummy residue capable of making the inlet valves of internal combustion engines faulty in their action. Monoolefines or chain hydrocarbons with only one double bond do not appear to possess these objectionable characters to such a high degree, and may be left in the spirit. This consideration should be noted, since the olefinic constituent of a cracked petrol is a high one, and complete removal would entail a heavy loss both in spirit and in sulphuric acid. Fractional removal of the di- and triolefines can be accomplished by scrubbing with 1 to 2 per cent of sulphuric acid.

Possible hydrogenation in solution by a catalytic process or in the vapour state at a low temperature suggests itself as a promising alternative.

Bone and Coward, on the other hand, advanced the nascent radical theory. On this view the hydrocarbon is considered to be at least momentarily split up into radicals, $\equiv CH$, $=CH_2$, and $-CH_3$, having a fugitive existence and undergoing immediate polymerisation to more

[1] *Compt. rend.*, 1866, **62**, 905; **63**, 788; and *Bull. Soc. Chim.*, 1867 (ii.), **7**, 251.
[2] *J. Chem. Soc.*, 1908, **93**, 1197.
[3] *Proc. Roy. Soc.*, 1871, **19**, 370.
[4] *J. f. Gasbeleucht.*, 1895, **39**, 377-830; *Ber.*, 1896, **29**, 2691.

complex hydrocarbons, usually, however, simpler than the original raw material.

The formation of a double bond is an endothermic reaction, the first stage of the cracking process thus requiring the continuous supply of a considerable amount of energy, in a paraffinoid hydrocarbon amounting to approximately 30,000 cals. per grm.-mol.

Rittman[1] has calculated the velocity constants of the typical cracking reaction, $C_2H_6 \longrightarrow C_2H_4 + H_2$, at various temperatures with the following results:

$$K\ 500° = 0{\cdot}027,$$
$$K\ 750° = 0{\cdot}074,$$
$$K\ 900° = 1{\cdot}28.$$

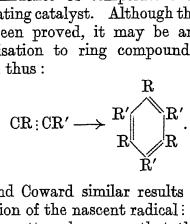
Thus, the rate of double bond formation or commencement of the cracking process of ethane is already quite appreciable at 600°.

The formation of a diolefine may be the result of the further elimination of hydrogen from a mono-olefine, or, according to Ostromisslenski,[2] due to thermal decomposition with the liberation of a paraffin hydrocarbon, thus:

$$CH_2 : CH \,.\, CH_2 \,.\, CH_2 \,.\, R \longrightarrow CH_2 : CH \,.\, CH : CH_2 + RH.$$

Thus far, we have shown how in the simple cracking process the production of gases, such as methane, hydrogen, the lower paraffin hydrocarbons, and the olefines, can be accounted for. Such products are usually obtained in the cracking of paraffin up to 600°, whilst, according to Rittman,[3] petrol formation may already be obtained at as low a temperature as 400°.

The formation of ring compounds.—According to Berthelot the formation of acetylene is possible in the process of degradation of a paraffin under the influence of temperature and pressure with or without a dehydrogenating catalyst. Although the presence of acetylene has never actually been proved, it may be argued that almost instantaneous polymerisation to ring compounds takes place at the cracking temperature, thus:



According to Bone and Coward similar results would be obtained by the rapid polymerisation of the nascent radical : CH.

It must not be forgotten, however, that the formation of stable ring compounds is also possible through the condensation of olefines or

[1] *J. Ind. Eng. Chem.*, 1915, **6**, 1029; **7**, 945; 1916, **8**, 20.
[2] *J. Russ. Phys. Chem. Soc.*, 1910, **42**, 145; 1915, **47**, 1947.
[3] *J. Ind. Eng. Chem.*, 1915 and 1916, **7**, 1019.

ehydrogenation of a triolefine. We have already noted that the rmation of polyolefines is possible in a cracking process, and our nowledge of the extraordinary reactivity of the system of conjugated uble bonds:

$$.C:C.C:C.,$$

ould lead us to suppose that cyclic condensation would probably ceed via a polyolefinic compound, and not through the hypothetical termediary formation of acetylene or of the still more nascent radical :CH. Ipatiew [1] has shown the formation of cyclohexane from heptane via α : n-hexylene, and Lebedev [2] the formation of the same mpound from erythrene.

Cyclic polymethylenes and aromatic hydrocarbons may thus result om processes of polymerisation of olefines, diolefines, and acetylenes, by the formation of closed rings from open chains by a process of ehydrogenation.

Since, whichever view be adopted, degradation has to proceed rther than in the preparation of petrols before the formation of clic compounds is possible, we would expect larger yields at higher acking temperatures and especially in the presence of dehydro-enating catalysts. The optimum temperature for aromatic hydro-rbons in practice is stated by Rittman to lie between 650° and 700°. or Baku petroleum, Smolenski, Turowicz, and Dobrowlski [3] report mperatures of 680°-720° C.; benzene, toluene, xylene, anthracene, and aphthalene are among the products. Above 800° thermal degradation carbon and hydrogen commences to be a source of trouble and ydrocarbon loss, partly due to the ultimate dissociation of methane, $CH_4 \rightleftarrows 2H_2 + C$, which is practically complete under 1 atmosphere ressure at 1200°.

It must not be forgotten that, owing to the complex composition the natural oil before cracking, the resulting product, when cracked any given temperature and pressure of operation, will also be complex. hus, the presence of ring compounds when petrol is desired or vice ersa, or the occurrence of a carbon deposition in the retorts, stills, or eel tubes, can scarcely be avoided.

For the general effect of temperature and pressure on cracking rocesses, as well as the relative advantages of cracking in the vapour liquid state, the reader is referred to the papers by Lomax, Dunstan, nd Thole cited above.

Dehydrogenation of cyclic compounds.—Sabatier and Senderens [4] owed that cyclohexane at a temperature of 270°-280° in the presence nickel underwent a process of dehydrogenation with the formation benzene and methane:

$$3C_6H_{12} \longrightarrow 2C_6H_6 + 6CH_4.$$

[1] *Ber.*, 1913, **46**, 1748.
[2] *J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1249.
[3] *J. Soc. Chem. Ind.*, 1922, **41**, 402A.
[4] *Compt. rend.*, 1897, **174**, 616.